

*Parallelized ab-initio calculation system
based on FMO*

PAICS

User Manual

Chapter 1

Compile and Execute

1.1 Compile

How to compile the *PAICS* is explained in this section.

1.1.1 Directory and file in the distribution

Directories and files included in the distribution of the *PAICS* are listed:

- **Makefile.paics**
Makefile for compiling the *PAICS*.
- **make.inc**
File used for compiling the *PAICS*. This file should be arranged according to your computer system.
- **make.sh**
Script to compile the *PAICS*.
- **clean.sh**
Script to clean up.
- **main.c**
Source code of the main function of the *PAICS*.
- **paics.run.sh**
An example of the script to run the *PAICS* with MPICH. This file should be arranged according to your computer system.

- `paics.run.lsf.sh`

An example of the script to run the *PAICS* with LSF. This file should be arranged according to your computer system.

- `man /`

Manuals (PDF) are stored. The following file exists.

`manual.pdf`

- `src /`

Source codes are stored. The following directories exist.

<code>include /</code>	header
<code>parallel_control /</code>	parallelization control
<code>memory_control /</code>	memory control
<code>paics /</code>	overall <i>PAICS</i>
<code>input /</code>	input
<code>output /</code>	output
<code>fmt /</code>	error function
<code>oneint /</code>	one-electron integral
<code>oneint_grad /</code>	derivation of one-electron integral
<code>eri /</code>	electron repulsion integral
<code>eri_grad /</code>	derivative of electron repulsion integral
<code>esp /</code>	environmental electrostatic potential
<code>projection /</code>	projection operator
<code>fragment /</code>	fragmentation
<code>monomer_scc /</code>	monomer scc calculation
<code>monomer /</code>	monomer calculation
<code>dimer_es /</code>	dimer-es calculation
<code>dimer /</code>	dimer calculation
<code>rhf /</code>	RHF
<code>cmp2 /</code>	canonical MP2
<code>ri_cmp2 /</code>	RI-MP2
<code>localize /</code>	localization of orbital
<code>lmp2 /</code>	local MP2

- `basis /`

Data files of basis set are stored. The following files exist.

<code>user.dat</code>	user definition
<code>sto3g.dat</code>	STO-3G

631g.dat	6-31G
631gdp.dat	6-31G**
cc-pVDZ.dat	cc-pVDZ
cc-pVTZ.dat	cc-pVTZ
cc-pVQZ.dat	cc-pVQZ
cc-pVDZso.dat	cc-pVDZ (segmented-opt)
cc-pVTZso.dat	cc-pVTZ (segmented-opt)
cc-pVDZri.dat	auxiliary basis function for cc-pVDZ
cc-pVTZri.dat	auxiliary basis function for cc-pVTZ
cc-pVQZri.dat	auxiliary basis function for cc-pVQZ

- sample /

Examples of the input and output are stored. The following files exist.

h2o-4.inp	conventional calculation of tetramer of H ₂ O
h2o-4.out	result of calculation
fmo-h2o-4.inp	FMO calculation of tetramer of H ₂ O
fmo-h2o-4.out	result of calculation
trp2.inp	conventional calculation of TPR-TRP
trp2.out	result of calculation
c12h26.inp	conventional calculation of C ₁₂ H ₂₆
c12h26.out	result of calculation
fmo-c12h26.inp	FMO calculation of C ₁₂ H ₂₆
fmo-c12h26.out	result of calculation
gly5.inp	conventional calculation of GLY ₅
gly5.out	result of calculation
fmo-gly5.inp	FMO calculation of GLY ₅
fmo-gly5.out	result of calculation
fmo-h2co-water12.inp	FMO calculation of H ₂ CO in water
fmo-h2co-water12.out	result of calculation
h2co-water12-pc.inp	conventional calculation of H ₂ CO in water
h2co-water12-pc.out	result of calculation
h2co-water128-pc.inp	conventional calculation of H ₂ CO in water
h2co-water128-pc.out	result of calculation
fmo-h2co-water128.inp	conventional calculation of H ₂ CO in water
fmo-h2co-water128.out	result of calculation
fmo-h2co-water128-pc.inp	conventional calculation of H ₂ CO in water
fmo-h2co-water128-pc.out	result of calculation
fmo-prp-gn8.inp	FMO calculation of print protein and GN8
fmo-prp-gn8.out	result of calculation

fmo-hiv-lpv.inp	FMO calculation of HIV1 protease and lorinavir
fmo-hiv-lpv.out	result of calculation
fmo-dna.inp	FMO calculation of DNA
fmo-dna.out	result of calculation

1.1.2 Compiler and library

For compile of the *PAICS*, MPI compiler and LAPACK libraries are needed.

1.1.3 Compile

1. modification of make.inc

Appropriate modification for your computer system should be made in the make.inc.

- ROOT_DIR
Absolute path of the root directory of the *PAICS*.
- CC
MPI compiler of C language.
- LIB
Libraries needed for the *PAICS*.
- PAICS_INCDIR
Directory containing the header files. Usually, this is set as

```
PAICS_INCDIR = ${ROOT_DIR}/src/include
```
- CFLAGS
Options of the compile. Usually, this is set as

```
CFLAGS = -c -O3 -I{PAICS_INCDIR}
```
- LFLAGS
Options of the link. This keyword depends on your computer system. Usually, this is not needed to be set.

2. run make.sh

Run make.sh in the root directory of the *PAICS*. If it is successful, main.exe is created. The compile takes time considerably.

1.2 Execute

How to execute the *PAICS* is explained in this section.

1.2.1 Make input file

When performing the *PAICS*, you need to make an input file (see the section of input of this manual).

1.2.2 Run calculation

1. You must set an environmental variable `PAICS_ROOT`, in which the root directory of the *PAICS* is set. (This environmental value is referred to during calculation).
2. Run the `main.exe` using MPI command together with one argument of the input filename.

Examples of the script to run the *PAICS* are shown in Figure 1.1.

1.2.3 Results of calculation

Results are printed out into standard output, so they could be recorded using redirection. After the calculation, you should check whether the **WARNING** has come out or not.

1.3 Test calculation

After the compilation, it is recommended to perform the test calculations and check the computational results as follows:

1.3.1 Execution of test calculations

To perform the test calculations is recommended with example inputs after the compilation. Since manner of the execution is depends on your computer systems, some trial and error may be needed. As a reference, computational times of the examples are shown below. These results are obtained without any change of the input file in the distribution.

- `h2o-4.inp`
 - 12 atoms, 96 basis functions, 1 fragment (RHF and RI-MP2 energy)
 - XeonE5429, 1 core (2.0 GByte memory per core)
 - time: 3.61 sec.
- `fmo-h2o-4.inp`
 - 12 atoms, 96 basis functions, 4 fragments (RHF and RI-MP2 energy)
 - XeonE5429, 1 core (2.0 GByte memory per core)
 - time: 2.56 sec.
- `trp2.inp`
 - 51 atoms, 516 basis functions, 1 fragment (RHF and RI-MP2 gradient)
 - XeonE5429, 1 core (2.0 GByte memory per core)
 - time: 13052.98 sec.

Figure 1.1: Examples of script to run *PAICS*

< in the case directly using mpirun (paics.run.sh) >

```
-----

#!/bin/bash

export PAICS_ROOT=/home/ishi/program/paics
INP=$1
NCPU=$2
DIR='pwd'

mpirun -np $NCPU $PAICS_ROOT/main.exe $DIR/$INP

-----
```

This script is executed as

```
% paics.run.sh [ input filename ] [ number of cores ] >& [ output filename ] &
```

< in the case using LSF (paics.run.lsf.sh) >

```
-----

#!/bin/bash

export PAICS_ROOT=/home/ishi/paics/paics-20080703-2
DIR='pwd'
BSUB_DIR=$DIR

INP_FILE=$1
OUT_FILE=$2
NCPU=$3

rm -f $BSUB_DIR/bsub.log
rm -f $BSUB_DIR/bsub.out

bsub -o $BSUB_DIR/bsub.out -e $BSUB_DIR/bsub.log -n $NCPU \
    "mpijob mpirun $PAICS_ROOT/main.exe $DIR/$INP_FILE >& $DIR/$OUT_FILE"

-----
```

This script is executed as

```
% paics.run.lsf.sh [ input filename ] [ output filename ] [ number of cores ]
```

- c12h26.inp
 - 38 atoms, 298 basis functions, 1 fragment (RHF and RI-MP2 energy)
 - XeonE5429, 1 core (2.0 GByte memory per core)
 - time: 250.80 sec.
- fmo-c12h26.inp
 - 38 atoms, 298 basis functions, 3 fragments (RHF and RI-MP2 energy)
 - XeonE5429, 1 core (2.0 GByte memory per core)
 - time: 288.36 sec.
- gly5.inp
 - 38 atoms, 379 basis functions, 1 fragment (RHF and RI-MP2 energy)
 - XeonE5429, 1 core (2.0 GByte memory per core)
 - time: 1242.73 sec.
- fmo-gly5.inp
 - 38 atoms, 379 basis functions, 3 fragments (RHF and RI-MP2 energy)
 - XeonE5429, 1 core (2.0 GByte memory per core)
 - time: 1034.30 sec.
- fmo-h2co-water12.inp
 - 40 atoms, 326 basis functions, 13 fragments (RHF, RI-MP2 and MP2 gradient)
 - XeonE5429, 1 core (2.0 GByte memory per core)
 - time: 302.36 sec.
- h2co-water12-pc.inp
 - 4 atoms, 38 basis functions, 1 fragment (RHF, RI-MP2 and MP2 gradient)
 - XeonE5429, 1 core (2.0 GByte memory per core)
 - time: 2.59 sec.
- fmo-h2co-water128.inp
 - 388 atoms, 3110 basis functions, 129 fragment (RHF and RI-MP2 gradient + electric field)
 - XeonE5429, 1 core (2.0 GByte memory per core)
 - time: 1276.88 sec.
- fmo-h2co-water128-pc.inp
 - 22 atoms, 182 basis functions, 7 fragments (RHF and RI-MP2 gradient + electric field)
 - XeonE5429, 1 core (2.0 GByte memory per core)
 - time: 51.32 sec.
- h2co-water128-pc.inp
 - 22 atoms, 182 basis functions, 1 fragment (RHF and RI-MP2 gradient + electric field)

- XeonE5429, 1 core (2.0 GByte memory per core)
- time: 112.41 sec.
- fmo-prp-gn8.inp
 - 1792 atoms, 16736 basis functions, 106 fragments (RHF and RI-MP2)
 - XeonE5429, 8 cores (2.0 Gbyte memory per core)
 - time: 114628.66 sec (31.8 hours)
- fmo-hiv-lpv.inp
 - 3225 atoms, 30224 basis functions, 203 fragments (RHF and RI-MP2)
 - XeonE5429, 8 cores (2.0 Gbyte memory per core)
 - time: 195976.17 sec (54.4 hours)
- fmo-dna.inp
 - 638 atoms, 6898 basis functions, 40 fragments (RHF and RI-MP2)
 - XeonE5429, 8 cores (2.0 Gbyte memory per core)
 - time: 28736.74 sec. (8.0 hours)

1.3.2 Check of result

Outputs corresponding to these inputs are also contained in distribution of the *PAICS*. Thus, you should compare between the your results and them.

[caution]

FMO calculation is progressed in order of the monomer SCC calculation, the monomer calculation, and the dimer calculation. The FMO-1 and FMO-2 properties are printed out with the time of the monomer and dimer calculations being finished, respectively. On the other hands, in conventional calculation, the monomer SCC and dimer calculations are not performed, and only one monomer calculation is performed. You should check that the tests calculations are progressed in such order by checking the output from a head, and confirm that the results of your calculations is in agreement with those of the output contained in the distribution of the *PAICS*.

Chapter 2

Input

2.1 General rule

The value of each keyword is set by writing a keyword name and value(s) separated with space or new-line.

- × `mpi_np = 4` Don't use "="
- `mpi_np 4` Use space

The line started with ' * ' is treated as a comment.

2.2 Keywords

In this section, keywords of the *PAICS* which are used in input are summarized.

2.2.1 General control

- `mpi_np` [`int`]

The number of cores used for calculation of each fragment or fragment pair. Default value is 1. For example, in the case that the total number of cores used for calculation is 8 and this keyword is set to 2, each calculation of fragment or fragment pair is parallelized with 2 cores, and 4 individual calculations are progressed at the same time. Thus, the total number of cores must be divisible by this value. You can set this value separately for monomer SCC calculation, monomer calculation, and dimer calculation using the following keywords. The total number of cores used for calculation is determined with MPI options when performing the calculation.

- `mpi_np_scc` [`int`]

The number of cores used for calculation of each fragment in monomer SCC calculation. If this keyword is not set, value of `mpi_np` keyword is used. In analogy with the `mpi_np`, the total number of cores used for calculation must be divisible by this value.

- `mpi_np_mon` [**int**]

The number of cores used for calculation of each fragment in monomer calculation. If this keyword is not set, value of `mpi_np` keyword is used. In analogy with the `mpi_np`, the total number of cores used for calculation must be divisible by this value.

- `mpi_np_dim` [**int**]

The number of cores used for calculation of each fragment pair in dimer calculation. If this keyword is not set, value of `mpi_np` keyword is used. In analogy with the `mpi_np`, the total number of cores used for calculation must be divisible by this value.

- `print_rank` [**int**]

MPI rank printing the results of calculation to standard output. Default value is 0. This keyword is used only for debug.

- `mem_mbyte` [**int**]

Size of memory per core used for calculation (Mbyte). Default value is 128. Since the default value is too small, this keyword should be set in every calculations.

- `lprint` [**int**]

General print level. You can decide the print level of each part of the calculation separately using the other keywords (see the following keywords).

- `coord_unit` [**int**]

Unit of the coordinates used in the input.

```
0 : bohr
1 : angstrom
```

Default is 0.

- `w_result_file` [**char**]

String used for name of the file, into which some information is written during calculation.

- `w_log_file` [**int**]

Write the results of calculation to the file by each core separately.

```
0 : not write
1 : write
```

Default value is 0. The file name is automatically determined as

```
[w_result_file]_[mpi_rank].log
```

Thus, when this keyword is set to 1, `w_result_file` keyword must be set. Since the results of each core is written separately, the file is made by the number of cores.

- `w_scc` [**int**]

Write the monomer density determined by the monomer scc calculation.

```
0 : not write
1 : write
```

Default value is 0. The file name is automatically determined as

```
[w_result_file].scc
```

Thus, when this keyword is set to 1, `w_result_file` keyword must be set. The electron density written to this file can be used as an initial density of the monomer SCC calculation when performing the other calculations.

- `r_result_file` [**char**]

String used for name of the file, from which some information is read during calculation.

- `r_scc` [**int**]

Read the monomer electron density from the file as an initial density of monomer scc calculation.

```
0 : not read
1 : read
```

Default value is 0. The file name is automatically determined as

```
[r_result_file].scc
```

Thus, when this keyword is set to 1, `r_result_file` keyword must be set.

- `atom`

Atoms are defined. This keyword must be given in every calculations. How to use this keyword is described in the following subsection.

- `fragment` [**int**]

Number of the fragments. This keyword must be given in every calculations. In the case of conventional calculation (i.e., not FMO calculation), this keyword is set to 1. How to use this keyword is described in the following subsection.

- **frag_atom**

Fragment is defined. This keyword must be given in all calculations. How to use this keyword is described in the following section.

- **basis_def**

Basis set is defined. How to use this keyword is described in the following section.

- **ex_point_charge**

External point charges are defined. After description of the number of point charges, the values and coordinates are given.

```
ex_point_charge [ number of point charges ]
  1 [ charge ] [ x ] [ y ] [ z ]
  2 [ charge ] [ x ] [ y ] [ z ]
    .
    .
    .
```

See example input (2.3.5).

- **position**

Positions are defined. For these positions, some field properties are calculated, i.e., electron density, electrostatic potential, and electric field. When this keyword is set, these field properties are automatically calculated. After description of the number of positions, the coordinates are given.

```
position [ number of positions ]
  1 [ x ] [ y ] [ z ]
  2 [ x ] [ y ] [ z ]
    .
    .
    .
```

See example input (2.3.5).

2.2.2 FMO method

- **scc_maxit** [**int**]

Maximum iteration number of the monomer SCC calculation. Default value is 199.

- **scc_tv_1** [**double**]

One of the threshold values used for convergence check of the monomer SCC calculation. When all the monomer energy changes become smaller than this value, the iteration is judged to be converged. Default value is $1.0\text{E}-6$. Both the values of **scc_tv_1** and **scc_tv_2** must be fulfilled for the convergence.

- `scc.tv.2` [**double**]

One of the threshold values used for convergence check of the monomer SCC calculation. When the total energy change (the FMO-1 energy change) become smaller than this value, the iteration is judged to be converged. Default value is $1.0\text{E}-6$. Both the values of `scc.tv.1` and `scc.tv.2` must be fulfilled for the convergence.

- `ldimer` [**double**]

Threshold value used for determination of the dimer-es approximation pairs. This value is given by the multiple of the van der Waals radius. When the distance of the nearest atoms between two fragments is larger than this value, its dimer calculation is performed using dimer-es approximation. Default value is 2.0.

- `lptc` [**double**]

Threshold value used for determination of the fragments treated with point charge approximation in calculation of the environmental electrostatic potential. This value is given by the multiple of the van der Waals radius. Default value is 2.0.

- `laoc` [**double**]

Threshold value used for determination of the fragments treated with three-center approximation in calculations of the environmental electrostatic potential. This value is given by the multiple of the van der Waals radius. Default value is 0.0.

- `projection.tv` [**double**]

Positive value used in the projection operators for the fragmentation. Default value is $1.0\text{E}+6$.

- `cp_corr` [**int**]

BSSE correction with the counter-poise method is applied for evaluations of the IFIE.

1 : apply
0 : not apply

Default value is 0. BSSE correction could be applied only for the IFIE of the fragment pairs not sharing covalent bonds.

- `scc.no_dyn` [**int**]

Dynamic update is used for acceleration of the monomer SCC convergence.

1 : not used.
0 : used.

Default value is 0.

- `frag_calc_pair [ int ] [ list ... ]`

Selection of the fragment pairs whose dimer calculations are performed. If not all the dimer calculations are performed, the total properties can not be evaluated (only interaction energies of the selected pairs are evaluated). This keyword is used as the follow:

```
frag_calc_pair [ number of the list of fragment pairs ]
               [ list 1 ]
               [ list 2 ]
               .
               .
               .
```

The [list] is a description specifying the fragment pairs. For example,

```
ifrag jfrag      ---> pair of ifrag and jfrag.
ifrag jfrag1-jfrag2 ---> pairs of ifrag and jfrag1-jfrag2.
ifrag ALL        ---> all pairs including ifrag.
```

See example input (2.3.6).

2.2.3 Molecular integral

- `eri_tv [ double ]`

Threshold value used for screening by K_{ab} in the two-electron integral evaluations. Default value is $1.0\text{E}-12$.

- `eri-cauchy_tv [ double ]`

Threshold value used for screening by Cauchy-Schwarz inequality in the two-electron integral evaluations. Default value is $1.0\text{E}-10$.

2.2.4 RHF

- `rhf [ int ]`

RHF calculation is performed.

```
1 : performed
0 : not performed
```

The default value is 1.

- `rhf_grad [ int ]`

RHF gradient calculation is performed.

```

1 : performed
0 : not performed

```

The default value is 0.

- **rhf_no_int_buff**

Two-electron integrals are buffered on memory in RHF calculation.

```

1 : buffered
0 : not buffered

```

Default value is 0. This value is applied for all monomer and dimer RHF calculations. This keyword is used only for checking performance of the program in development.

- **rhf_lprint_1** [**int**]

Print level of monomer RHF calculation. Default value is -1, which gives a normal printing.

- **rhf_lprint_2** [**int**]

Print level of dimer RHF calculation. Default value is -1, which gives a normal printing.

- **rhf_maxit** [**int**]

Maximum number of RHF iteration. Default value is 999. This value is applied for all monomer and dimer RHF calculations.

- **rhf_ndiis** [**int**]

Number of Fock matrices recorded for DIIS acceleration. Default value is 4. This value is applied for all monomer and dimer RHF calculations.

- **rhf_diis_tv** [**double**]

Threshold value used for DIIS acceleration. When the maximum value of the DIIS error vectors become smaller than this value, DIIS acceleration is started. Default value is 2.0. This value is applied for all monomer and dimer RHF calculations.

- **rhf_orth** [**int**]

Method used for the orthogonalization of the basis function.

```

0 : canonical orthogonalization.
1 : symmetric orthogonalization.

```

Default value is 1. This value is applied for all monomer and dimer RHF calculations.

- **rhf_init_mo** [**int**]

Method for making initial orbitals.

```

0 : hcore
1 : projection from orbitals using sto-3g

```

Default value is 1. This value is applied for all monomer and dimer RHF calculations.

- **rhf_orth_tv** [**double**]

Threshold value used for canonical orthogonalization. Default value is 1.0E−6. This value is applied for all monomer and dimer RHF calculations.

- **rhf_eng_tv** [**double**]

Threshold value of the energy used for the convergence test. Default value is 1.0E−8. This value is applied for all the monomer and dimer RHF calculations.

2.2.5 Canonical MP2

- **cmp2** [**int**]

Canonical MP2 calculation is performed.

```

0 : not performed
1 : performed

```

Default value is 0.

- **cmp2_grad** [**int**]

MP2 gradient calculation is performed.

```

1 : performed
0 : not performed

```

Default value is 0.

- **cmp2_lprint_1** [**int**]

Print level of monomer canonical MP2 calculation. Default value is -1, which gives a normal printing.

- **cmp2_lprint_2** [**int**]

Print level of dimer canonical MP2 calculation. Default value is -1, which gives a normal printing.

- **cmp2_th_iajs** [**double**]

Threshold value used for screening of the integral transformation. Default value is 1.0E−8.

- `cmp2_th_iars` [**double**]

Threshold value used for screening of the integral transformation. Default value is $1.0\text{E}-8$.

- `cmp2_th_pqrs` [**double**]

Threshold value used for screening of the integral transformation. Default value is $1.0\text{E}-8$.

2.2.6 RI-MP2

- `ri_cmp2` [**int**]

RI-MP2 calculation is performed.

```
0 : not performed
1 : performed
```

Default value is 0. In RI-MP2 calculation, auxiliary basis function is used. In the *PAICS*, auxiliary basis function is automatically selected.

```
cc-pVDZri ← cc-pVDZ, cc-pVDZso, 6-31G, 6-31G**.
cc-pVTZri ← cc-pVTZ.
```

- `ri_cmp2_grad` [**int**]

RI-MP2 gradient calculation is performed.

```
1 : performed
0 : not performed
```

Default value is 0.

- `ri_cmp2_lprint_1` [**int**]

Print level of monomer RI-MP2 calculation. Default value is -1, which give a normal printing.

- `ri_cmp2_lprint_2` [**int**]

Print level of dimer RI-MP2 calculation. Default value is -1, which give a normal printing.

2.2.7 Local MP2

- `lmp2_chk` [**int**]

Local MP2 calculation is performed.

```

0 : not performed
1 : performed

```

Default value is 0. The local MP2 calculation in the **PAICS** is used not for speed-up but for fragment interaction analysis based on local MP2 (FILM).

- **lmp2_lprint_1** [**int**]

Print level of monomer local MP2 calculation. Default value is -1, which gives a normal printing.

- **lmp2_lprint_2** [**int**]

Print level of dimer local MP2 calculation. Default value is -1, which gives a normal printing.

- **lmp2_loc** [**int**]

Method of localization.

```

0 : Pipek-Mezey
1 : Boys
2 : not perform localization

```

Default value is 0 (the value of 2 is used only for the debug).

- **lmp2_max_itr** [**int**]

Maximum iteration number for solving linear equation. Default value is 30.

- **lmp2_th_1** [**double**]

Threshold value used for determination of the domain. Default value is 0.02.

- **lmp2_th_1_dim** [**double**]

Threshold value used for determination of the domain. Default value is 0.001.

- **lmp2_th_2** [**double**]

Threshold value used for selection of the orbital pair. Default value is 4.0.

- **lmp2_th_2_dim** [**double**]

Threshold value used for selection of the orbital pair. Default value is 8.0.

- **lmp2_th_3** [**double**]

Threshold value used for integral transformation. Default value is 0.004.

- **lmp2_th_4** [**double**]

Threshold value used for integral transformation. Default value is 1.0E-12.

2.2.8 "atom" keyword

Atoms are defined using `atom` keyword.

```
-----
ATOM
[ a ] [ b ]
[ c ] [ d ] [ e ] [ x ] [ y ] [ z ]
[ c ] [ d ] [ e ] [ x ] [ y ] [ z ]
.
.
.
-----
```

where each column is

```
[ a ]  Number of atoms
[ b ]  Type of basis set
       0 : cartesian type
       1 : spherical type

[ c ]  Sequential serial number
[ d ]  Atomic number
[ e ]  Name of basis function.
[ x ]  X-coordinate
[ y ]  Y-coordinate
[ z ]  Z-coordinate
```

The "name of basis function" is defined with `basis_def` keyword. The coordinates of the atoms are give in the unit which is defined with `coord_unit` keyword. See example inputs (2.3).

2.2.9 "frag_atom" keyword

Number of the fragment is defined using `fragment` keyword, and each fragment is defined using `frag_atom` keyword. Thus, the number of `frag_atom` keywords in the input should be same as the number of the fragments. The format is

```
-----
FRAGMENT
  [ number of fragment ]

FRAG_ATOM [ a ] [ b ] [ c ]
  [ d ] [ d ] [ d ] [ d ] [ d ] [ d ] . . . . .
  [ e ] [ e ] . . .

FRAG_ATOM [ a ] [ b ] [ c ]
  [ d ] [ d ] [ d ] [ d ] [ d ] [ d ] . . . . .
  [ e ] [ e ] . . .

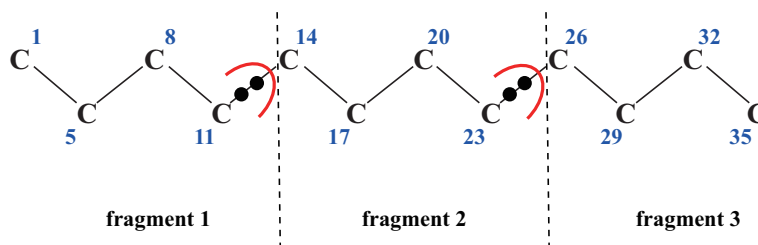
FRAG_ATOM [ a ] [ b ] [ c ]
  .
  .
  .
-----
```

where each column is

- [a] Formal charge of the fragment
- [b] Number of atoms in the fragment
- [c] Number of atoms added to the fragment
- [d] Sequential serial number of the atoms in the fragment
- [e] Sequential serial number of the atoms added to the fragment

The "atom added to the fragment" is the atoms in the other fragment. But, to achieve appropriate fragmentation with cutting covalent bonds, portion of the nucleus charge and basis function of the atoms in the neighboring fragment is added into the fragment when performing the monomer and dimer calculations. Here, such atoms are called "atom added to the fragment". Definition of the fragment is very complicated, so an illustrative example is given. In Figure 2.1, the fragmentation of $C_{12}H_{26}$ is showed.

Figure 2.1: An illustrative example of the fragmentation. The numbers in the figure are the sequential serial numbers of the atoms. This is $C_{12}H_{26}$ molecule (the hydrogen atoms are omitted).



The definition of the fragmentation in Figure 2.1 is

```

-----
FRAGMENT
  3

FRAG_ATOM  0  13  1
            1  2  3  4  5  6  7  8  9  10  11  12  13
            14

FRAG_ATOM  0  12  1
            14 15 16 17 18 19 20 21 22 23 24 25
            26

FRAG_ATOM  0  13  0
            26 27 28 29 30 31 32 33 34 35 36 37 38
-----

```

Although 14th atom is not an atom in the fragment 1, an positive charge (+1.0 e) and basis function of this atom are included in the calculation of the fragment 1 to achieve an appropriate fragmentation. Thus, for the definition of the fragment 1, 14th atom is treated as the "atom added to the fragment". Similarly, 26th atom is the "atom added to the fragment" for the fragment 2. For the fragment 3, the "atom added to the fragment" dose not exist.

2.2.10 "basis_def" keyword

Basis set is defined using **basis_def** keyword. But, in calculations using the basis functions ready defined in the *PAICS*, this keyword is not needed. The format of **basis_def** keyword is

```

-----
BASIS_DEF
  [ a ]
  [ b ]
  [ c ]  [ d ]
        [ e ]  [ f ]  [ g ]
        .
        .

  [ c ]  [ d ]
        [ e ]  [ f ]  [ g ]
        .
        .

  [ c ]  [ d ]
        .
        .
-----

```

where each column is

- [a] Name of definition
- [b] Number of shells
- [c] Angular momentum
- [d] Number of contraction
- [e] Sequential serial number of primitive gaussian
- [f] coefficient of primitive gaussian
- [g] exponential of primitive gaussian

The "name of definition" is used in **atom** keyword to determine the basis function of each atom. Because this definition is complicated, an example of the cc-pVDZ basis set of carbon atom is given in Figure 2.2.

Figure 2.2: Definition of the cc-pVDZ basis set of carbon atom.

```

BASIS_DEF
cc-pVDZ_006
6
0      8
      1      0.0006920      6665.0000000
      2      0.0053290      1000.0000000
      3      0.0270770      228.0000000
      4      0.1017180      64.7100000
      5      0.2747400      21.0600000
      6      0.4485640      7.4950000
      7      0.2850740      2.7970000
      8      0.0152040      0.5215000
0      8
      1      -0.0001460      6665.0000000
      2      -0.0011540      1000.0000000
      3      -0.0057250      228.0000000
      4      -0.0233120      64.7100000
      5      -0.0639550      21.0600000
      6      -0.1499810      7.4950000
      7      -0.1272620      2.7970000
      8      0.5445290      0.5215000
0      1
1      1      1.0000000      0.1596000
      3
      1      0.0381090      9.4390000
      2      0.2094800      2.0020000
      3      0.5085570      0.5456000
1      1
2      1      1.0000000      0.1517000
      1
      1      1.0000000      0.5500000

```

In this example, the name of the definition is `cc-pVDZ_006`. When `cc-pVDZ_006` is used in `atom` keyword, this basis set is applied. The basis sets ready defined in the *PAICS* are shown in the following table.

basis set	name of definition	available atoms
STO-3G	STO-3G_???	??? = 001 ~ 053
6-31G	6-31G_???	??? = 001 ~ 030
6-31G**	6-31G**_???	??? = 001 ~ 030
cc-pVDZ	cc-pVDZ_???	??? = 001 ~ 018, 020 ~ 036
cc-pVTZ	cc-pVTZ_???	??? = 001 ~ 018, 020 ~ 036
cc-pVQZ	cc-pVQZ_???	??? = 001 ~ 018, 020 ~ 036
cc-pVDZso	cc-pVDZso_???	??? = 001 ~ 018, 031 ~ 036
cc-pVTZso	cc-pVTZso_???	??? = 001 ~ 018, 031 ~ 036
cc-pVDZri	cc-pVDZri_???	??? = 001 ~ 018, 031 ~ 036
cc-pVTZri	cc-pVTZri_???	??? = 001 ~ 018, 031 ~ 036

2.3 Example

In this section, some examples of the input are given. These input files are included in the distribution of the *PAICS*.

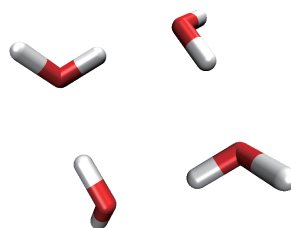
2.3.1 Conventional calculation of tetramer of water molecules

In Figure 2.3, input for the conventional calculation of tetramer of water molecules is given. In the case of a conventional calculation (not FMO calculation), one definition of the fragment must be given. When performing such a calculation, one monomer calculation is performed, on the other hands monomer scc and dimer calculations are skipped. The meaning of each line of the input:

Figure 2.3: Example input (h2o-4.inp)

```

1 :
2 : mpi_np 1
3 : mem_mbyte 1792
4 :
5 : ri_cmp2 1
6 :
7 : ATOM
8 :      12      1
9 :      1 8 cc-pVDZso_008 -3.486380 1.544957 0.147898
10 :     2 8 cc-pVDZso_008 1.544970 3.486131 -0.147941
11 :     3 8 cc-pVDZso_008 3.486367 -1.544968 0.147896
12 :     4 8 cc-pVDZso_008 -1.544966 -3.486182 -0.147916
13 :     5 1 cc-pVDZso_001 -1.941779 2.463103 0.002632
14 :     6 1 cc-pVDZso_001 -4.427908 2.291387 1.463627
15 :     7 1 cc-pVDZso_001 2.463369 1.941622 -0.003213
16 :     8 1 cc-pVDZso_001 2.291661 4.428602 -1.462845
17 :     9 1 cc-pVDZso_001 1.941777 -2.463141 0.002634
18 :    10 1 cc-pVDZso_001 4.427776 -2.291180 1.463833
19 :    11 1 cc-pVDZso_001 -2.463453 -1.941764 -0.002780
20 :    12 1 cc-pVDZso_001 -2.291353 -4.428135 -1.463364
21 :
22 : FRAGMENT
23 :      1
24 :
25 : FRAG_ATOM      0      12      0
26 :      1 2 3 4 5 6 7 8 9 10 11 12
27 :
28 :
```



- line: 02** This line sets the number of cores user for monomer or dimer calculation. In the case of a conventional calculation, only one monomer calculation is performed. Thus, this number should be same as the total number of cores used in calculation. The total number of cores is given when performing calculation with the MPI option.
- line: 03** This line sets the size of memory per core used for calculation in Mbyte. In this case, 1729 Mbyte is used per core.
- line: 05** This line sets performing RI-MP2 calculation. Note that RHF calculation is performed by default.
- line: 07-08** These lines mean that atomic numbers, coordinates, basis functions of 12 atoms are given in the following lines. The number of 1 in this line indicates that spherical harmonic type of basis function is used.
- line: 09-20** These line give the atomic numbers, coordinates, basis functions of the atoms.
- line: 22-23** These lines give the number of the fragment. In this case, only one fragment is given because the conventional calculation is performed.

line: 25–26 These lines give the definition of the fragment. In this case, only one definition of the fragment is given.

2.3.2 FMO calculation of tetramer of water molecules

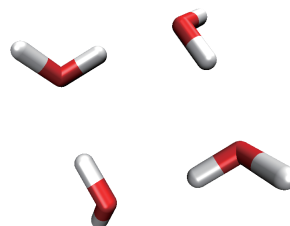
In Figure 2.4, input for FMO calculation of tetramer of water molecules is given. The

Figure 2.4: Example input (fmo-h2o-4.inp)

```

1 :
2 : mpi_np 1
3 : mem_mbyte 1792
4 :
5 : ri_cmp2 1
6 :
7 : ATOM
8 :      12      1
9 :      1 8 cc-pVDZso_008 -3.486380 1.544957 0.147898
10 :     2 8 cc-pVDZso_008 1.544970 3.486131 -0.147941
11 :     3 8 cc-pVDZso_008 3.486367 -1.544968 0.147896
12 :     4 8 cc-pVDZso_008 -1.544966 -3.486182 -0.147916
13 :     5 1 cc-pVDZso_001 -1.941779 2.463103 0.002632
14 :     6 1 cc-pVDZso_001 -4.427908 2.291387 1.463627
15 :     7 1 cc-pVDZso_001 2.463369 1.941622 -0.003213
16 :     8 1 cc-pVDZso_001 2.291661 4.428602 -1.462845
17 :     9 1 cc-pVDZso_001 1.941777 -2.463141 0.002634
18 :    10 1 cc-pVDZso_001 4.427776 -2.291180 1.463833
19 :    11 1 cc-pVDZso_001 -2.463453 -1.941764 -0.002780
20 :    12 1 cc-pVDZso_001 -2.291353 -4.428135 -1.463364
21 :
22 : FRAGMENT
23 :      4
24 :
25 : FRAG_ATOM 0 3 0
26 :      1 5 6
27 :
28 : FRAG_ATOM 0 3 0
29 :      2 7 8
30 :
31 : FRAG_ATOM 0 3 0
32 :      3 9 10
33 :
34 : FRAG_ATOM 0 3 0
35 :      4 11 12
36 :
37 :

```



meaning of each line of the input:

line: 02 This line sets the number of cores user for each monomer or dimer calculation. In this case, all the monomer and dimer calculations are performed with one core, and individual calculations are progressed at the same time.

line: 03 This line sets the size of memory per core used for calculation in Mbyte.

line: 05 This line sets performing RI–MP2 calculation.

line: 07–08 These lines mean that atomic numbers, coordinates, basis functions of 12 atoms are given in the following lines, and spherical harmonic basis functions are used.

line: 09–20 These line give the atomic number, coordinates, basis functions of the atoms.

line: 22–23 These lines give the number of fragment. In this case, 4 fragments are given in the following lines.

line: 25–35 These lines give the definition of the 4 fragments.

2.3.3 FMO calculation of (GLY)₅

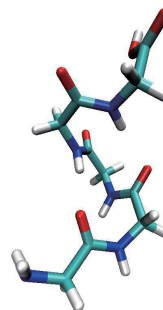
In Figure 2.5, input for FMO calculation of (GLY)₅ is given. The meaning of each line

Figure 2.5: Example input (fmo-gly5.inp)

```

1 :
2 : mpi_np 1
3 : mem_mbyte 1792
4 :
5 : ri_cmp2 1
6 :
7 : ATOM
8 :      38      1
9 :      1  7  cc-pVDZso_007 -8.627555 -4.276962  2.760481
10 :      2  6  cc-pVDZso_006 -8.859925 -2.857283  0.461630
11 :      3  6  cc-pVDZso_006 -6.396634 -1.768013 -0.560757
12 :      4  8  cc-pVDZso_008 -4.376048 -2.217524  0.372588
13 :      5  1  cc-pVDZso_001 -7.403302 -5.700198  2.541971
14 :
15 :
16 :
17 :
18 :
19 :
20 :
21 :
22 :
23 :
24 :
25 :
26 :
27 :
28 :
29 :
30 :
31 :
32 :
33 :
34 :
35 :
36 :
37 :
38 :
39 :
40 :
41 :
42 : 34  1  cc-pVDZso_001  2.627541  0.136631 -0.932746
43 : 35  1  cc-pVDZso_001  5.491791 -4.541737 -1.266959
44 : 36  1  cc-pVDZso_001  4.745658 -2.453913 -3.720098
45 : 37  8  cc-pVDZso_008  8.395797  0.629437 -0.701933
46 : 38  1  cc-pVDZso_001 10.133232  1.059911 -0.772473
47 :
48 :
49 : FRAGMENT
50 :      3
51 :
52 : FRAG_ATOM      0      13      0
53 :      1  2  3  4  5  6  7  8  9 10 13 14 15
54 :
55 : FRAG_ATOM      0      14      1
56 :      11 12 16 17 18 19 20 21 22 23 24 27 28 29
57 :      10
58 :
59 : FRAG_ATOM      0      11      1
60 :      25 26 30 31 32 33 34 35 36 37 38
61 :      24
62 :

```



is

line: 02 This line sets the number of cores user for each monomer or dimer calculation. In this case, all the monomer and dimer calculations are performed with one core, and individual calculations are progressed at the same time.

line: 03 This line sets the size of memory per core used for calculation in Mbyte.

line: 05 This line sets performing RI-MP2 calculation.

line: 07–08 These lines mean that atomic numbers, coordinates, basis functions of 38 atoms are given in the following lines, and spherical harmonic basis functions are used.

line: 09–46 These line give the atomic number, coordinates, basis functions of the atoms.

line: 49–50 These lines give the number of fragment. In this case, 3 fragments are given in the following lines.

line: 52–61 These lines give the definition of the 3 fragments.

2.3.4 FMO calculation of H₂CO in water molecules

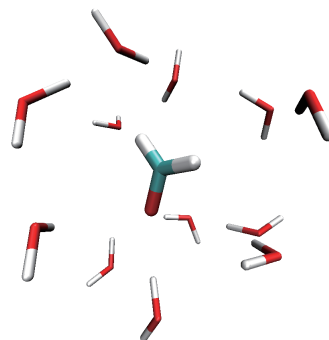
In Figure 2.6, input for FMO calculation of H₂CO in water molecules is given. The meaning of each line of the input:

Figure 2.6: Example input (fmo-h2co-water12.inp)

```

1 :
2 : mem_mbyte 1792
3 : mpi_np 1
4 :
5 : cmp2_grad 1
6 : ri_cmp2_grad 1
7 :
8 : ATOM
9 :
10 : 1 8 0.319322 -1.256692 -0.106102
11 : 2 6 -0.904629 0.307596 -1.387482
12 : 3 1 -0.117246 1.047770 -3.137662
13 : 4 1 -2.682198 0.940018 -0.700446
14 : 5 8 -0.103300 5.492608 -4.334387
15 :
16 :
17 :
18 :
19 :
20 :
21 :
22 :
23 :
24 :
25 :
26 :
27 :
28 :
29 :
30 :
31 :
32 :
33 :
34 :
35 :
36 :
37 :
38 :
39 :
40 :
41 :
42 :
43 :
44 :
45 : 36 1 -8.052276 2.267906 0.972153
46 : 37 1 -5.366306 -1.949235 2.692752
47 : 38 8 -1.972834 -2.503713 -7.637485
48 : 39 1 -2.238241 -0.671106 -7.162132
49 : 40 1 -2.455521 -3.946313 -6.359779
50 :
51 : FRAGMENT
52 : 13
53 :
54 : FRAG_ATOM 0 0 4 0
55 : 1 2 3 4
56 :
57 : FRAG_ATOM 0 3 0
58 : 5 6 8
59 :
60 :
61 :
62 :
63 :
64 :
65 :
66 :
67 :
68 :
69 :
70 :
71 :
72 :
73 :
74 :
75 :
76 :
77 :
78 :
79 :
80 :
81 :
82 :
83 :
84 :
85 :
86 :
87 :
88 :
89 :
90 : FRAG_ATOM 0 3 0
91 : 38 39 40
92 :

```



line: 02 This line sets the number of cores user for each monomer or dimer calculation. In this case, all the monomer and dimer calculations are performed with one core, and individual calculations are progressed at the same time.

line: 03 This line sets the size of memory per core used for calculation in Mbyte.

line: 05–06 This lines sets performing canonical MP2 and RI–MP2 gradient calculations. By these two lines, energy and gradient calculations of RHF, canonical MP2, RI–MP2 are performed.

line: 08–49 These line give the atomic numbers, coordinates, basis functions of the 40 atoms.

line: 51–91 These lines give the definition of the 13 fragments (one H₂CO and 12 water molecules).

2.3.5 Conventional calculation of H₂CO with external point charges

In Figure 2.7, input for the conventional calculation of H₂CO in water molecules is given, where the water molecules are treated as external point charge. The meaning of each line of the input:

line: 02 This line sets the number of cores user for monomer calculation.

line: 03 This line sets the size of memory per core used for calculation in Mbyte.

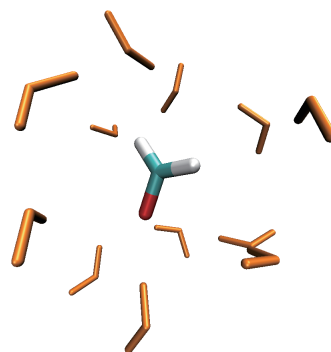
line: 05–06 This lines sets performing canonical MP2 and RI–MP2 gradient calculations. By these two lines, energy and gradient calculations of RHF, canonical MP2, RI–MP2 are performed.

Figure 2.7: Example input (h2co-water12-pc.inp)

```

1 :
2 : mem_mbyte 1792
3 : mpi_np 1
4 :
5 : cmp2_grad 1
6 : ri_cmp2_grad 1
7 :
8 : ATOM
9 :
10 : 1 8 cc-pVDZso_008 0.319322 -1.256692 -0.106102
11 : 2 6 cc-pVDZso_006 -0.904629 0.307596 -1.387482
12 : 3 1 cc-pVDZso_001 -0.117246 1.047770 -3.137662
13 : 4 1 cc-pVDZso_001 -2.682198 0.940018 -0.700446
14 :
15 : ex_point_charge
16 : 36
17 : 1 -0.295544 -0.103300 5.492608 -4.334387
18 : 2 0.204929 -0.317599 7.022772 -5.412113
19 : 3 0.180917 -2.521898 6.514663 -1.099571
20 :
21 :
22 :
23 :
24 :
25 :
26 :
27 :
28 :
29 :
30 :
31 :
32 :
33 :
34 : -0.558942 -1.972834 -2.503713 -7.637485
35 : 0.210549 -2.238241 -0.671106 -7.162132
36 : 0.236426 -2.455521 -3.946313 -6.359779
37 :
38 : position
39 : 36
40 : 1 -0.103300 5.492608 -4.334387
41 : 2 -0.317599 7.022772 -5.412113
42 : 3 -2.521898 6.514663 -1.099571
43 :
44 :
45 :
46 :
47 :
48 :
49 :
50 : 34 -1.972834 -2.503713 -7.637485
51 : 35 -2.238241 -0.671106 -7.162132
52 : 36 -2.455521 -3.946313 -6.359779
53 :
54 : FRAGMENT
55 : 1
56 :
57 : FRAG_ATOM 2 0 3 4 0
58 :
59 :
60 :

```



line: 08–13 These lines give the atomic numbers, coordinates, basis functions of the 4 atoms in H_2CO molecule.

line: 15–16 These lines mean that 36 external point charges are given in the following lines.

line: 17–52 These lines give the 36 external point charges corresponding to 12 water molecules.

line: 54–55 These lines mean that 36 position are given in the following lines.

line: 56–91 These lines give the 36 positions where the electron density, electrostatic potential, and electric field are calculated.

line: 93–97 These lines give the definition of one fragments of H_2CO .

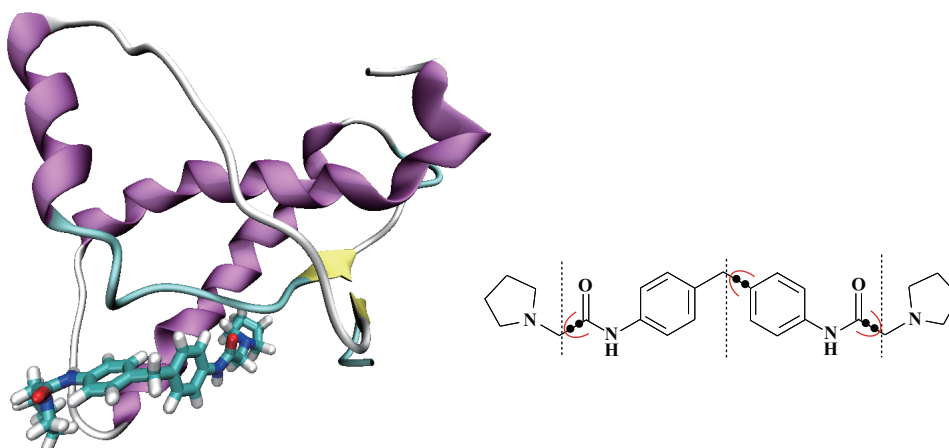
2.3.6 FMO calculation of print protein with GN8 molecule

In Figure 2.8, input of the FMO calculation of print protein and GN8 molecule is given, in which each amino acid residue is treated as a single fragment, and GN8 molecule is divided into 4 fragments. The meaning of each line of the input:

line: 0002–0004 These lines set the number of cores user for the monomer SCC calculation, the monomer calculation, and the dimer calculation. In this case, all monomer calculations are performed with 8 cores in the monomer SCC procedure. On the other hands, if the total cores used for this calculation is 8, all monomer and dimer

Figure 2.8: fmo-prp-gn8.inp

```
1 :  
2 : mpi_np_scc 8  
3 : mpi_np_mon 1  
4 : mpi_np_dim 1  
5 : mem_mbyte 1792  
6 :  
7 : ri_cmp2 1  
8 :  
9 : ATOM  
10 :      1729      1  
11 :      1 7 cc-pVDZso_007 43.057410 76.048248 80.942639  
12 :      2 1 cc-pVDZso_001 44.179907 75.949983 82.482766  
13 :      3 1 cc-pVDZso_001 43.216147 74.423084 79.954312  
14 :      4 1 cc-pVDZso_001 41.247052 76.295803 81.494439  
15 :      5 6 cc-pVDZso_006 43.828418 78.174190 79.332592  
.  
.  
.  
1735 : 1725 1 cc-pVDZso_001 74.517570 59.611411 109.392466  
1736 : 1726 1 cc-pVDZso_001 75.199761 58.160101 112.366895  
1737 : 1727 6 cc-pVDZso_006 76.511231 56.081402 109.069323  
1738 : 1728 1 cc-pVDZso_001 77.344601 54.760484 110.420477  
1739 : 1729 1 cc-pVDZso_001 77.996556 57.143428 108.103673  
1740 :  
1741 :  
1742 : FRAGMENT  
1743 :      106  
1744 :  
1745 : FRAG_ATOM      1      7      0  
1746 :      5 1 2 3 4 6 7  
1747 :  
1748 : FRAG_ATOM      0      19      1  
1749 :     12 10 11 13 14 15 16 17 18 19 20 21 22 23 24 25 26 8 9  
1750 :      5  
.  
.  
.  
2177 : FRAG_ATOM      0      14      2  
2178 :     1700 1701 1702 1703 1709 1707 1705 1706 1708 1710 1711 1712 1713 1704  
2179 :     1697 1714  
2180 :  
2181 : FRAG_ATOM      0      17      1  
2182 :     1683 1684 1685 1686 1687 1688 1689 1690 1696 1694 1692 1693 1695 1697 1698 1699 1691  
2183 :     1680  
2184 :  
2185 : FRAG_ATOM      0      16      0  
2186 :     1667 1668 1669 1670 1671 1672 1673 1674 1675 1676 1677 1678 1679 1680 1681 1682  
2187 :
```



calculations are performed with 1 core, and 8 individual calculations are progressed at the same time.

line: 0005 This line sets the size of memory per core used for calculation in Mbyte.

line: 0007 This line sets performing RI-MP2 calculations.

line: 0009–1739 These lines give the atomic numbers, coordinates, basis functions of 1792 atoms, and spherical type basis sets are used.

line: 1742–2186 These lines give the definitions of 106 fragments.

If only the interaction energies between prion protein and GN8 are needed, just performing the selected dimer calculations is enough. Using `frag_calc_pair` keyword, only selected dimer calculations are performed. In this case, prion protein and GN8 is assigned to 1–102 and 103–106 fragments, respectively. Thus, the following descriptions should be added to the input.

```
frag_calc_pair 1
103-106 1-102
```

This is equivalent to the following descriptions.

<pre>frag_calc_pair 4 103 1-102 104 1-102 105 1-102 106 1-102</pre>	<pre>frag_calc_pair 408 103 1 103 2 . . 103 102 104 1 104 2 . . 104 102 105 1 105 2 . . 105 102 106 1 106 2 . . 106 102</pre>
---	---

2.3.7 The other examples of input

The other examples are included in the distribution of *PAICS*, which are listed as follows.

- `trp2.inp`
conventional calculation of (TRP)₂.

- c12h26.inp
conventional calculation of C₁₂H₂₆ molecule.
- fmo-c12h26.inp
FMO calculation of C₁₂H₂₆ molecule.
- gly5.inp
conventional calculation of (GLY)₅.
- fmo-h2co-water128.inp
MO calculation of H₂CO in water molecules.
- fmo-h2co-water128-pc.inp
FMO calculation of H₂CO in water molecules with point charges.
- h2co-water128-pc.inp
conventional calculation of H₂CO in water molecules with point charges.
- fmo-hiv-lpv.inp
FMO calculation of HIV1 protease and lopinavir molecule.
- fmo-dna.inp
FMO calculation of DNA.

2.3.8 Development of the program for making the input (*PaicsView*)

As shown in this section, it is not easy to make an input manually in the case of the FMO calculation of a protein or nucleic acid. Now, we have developed the program, *PaicsView*, which supports creation of an input of the *PAICS*. In the near future, the source code of *PaicsView* is going to be open to the public.

Chapter 3

Output

3.1 Overall of the output

In the *PAICS*, progress and result of calculation are printed out to the standard output by the following order:

1. **input information**

Values of the keyword, definitions of the basis set, coordinates of the nuclei and basis functions, and definition of the fragment are printed out.

2. **make projection operator**

Information about making projection operators used for fragmentation. In the *PAICS*, the projection operators are created in every calculations.

3. **memory information**

Size of the memory for the global variables of the *PAICS*.

4. **fragment information**

Information of the fragments.

5. **fragment pair information**

Information of the fragment pairs.

6. **monomer scc calculation**

Progress of the monomer SCC calculation.

7. **monomer scc result**

Results of the monomer SCC calculation.

8. **monomer calculation**

Progress of each monomer calculation. Only monomer calculations performed with the core whose `mpi_rank` is 0 are printed out.

9. **fmo-1 result**

Values evaluated using the result of monomer calculations (i.e., the results of one-body approximation of the FMO method).

10. **dimer-es approximatoin**

Progress of the dimer-es approximation.

11. **dimer calculation**

Progress of each dimer calculation. Only dimer calculations performed with the core whose `mpi_rank` is 0 are printed out.

12. **fmo-2 result**

Values evaluated using the results of monomer and dimer calculations (i.e., the results of two-body approximation of the FMO method).

3.2 Input information

After the following keyword, information about the input are printed out:

```
=====
input information
=====
```

- < memory >
- < mpi parallel >
- < parameters and thresholds >
- < rhf >
- < cmp2 >
- < ri-cmp2 >
- < lmp2 >
- < read basis set definition >
- < input coordinate of nucleus charge >
- < input coordinate of basis sets >
- < input fragment >

3.3 Make projection operator

In the *PAICS*, before beginning the monomer SCC calculation, RHF calculations and orbital localizations of a CH₄ molecule are performed for every fragmentations including cut of a covalent bond to make a projection operator. After the following keyword, information about the making projection orbital are printed out:

```
=====
make projection operator
=====
```

If the fragmentations including cut of a covalent bond exist, information about the RHF calculation and the localization to make projection operator is printed out.

3.4 Memory information

After the following keyword, information about the global variables of the *PAICS* are printed out:

```
=====
memory information
=====
```

The size of the memory used for the global variables is printed out. The remaining memory can be used for the following quantum chemical calculations. Additionally, names of the variables which use the memory more than 1024 Kbyte.

3.5 Fragment information

After the following keyword, information about each fragment is printed out:

```
=====
fragment information
=====
```

Information of the fragments are printed out to order with large size, which include number of the basis functions, electrons, and projection orbitals. The number of fragments treated in three approximation levels (i.e., 4-center integrals, 3-center integrals, and point-charge) when calculating the environmental electrostatic potential are printed out for each fragment. Additionally, the number of fragments calculated with and without dimer-es approximation when performing dimer calculation are also printed out for each fragment.

3.6 Fragment pair information

After the following keyword, several informations about the fragment pairs are printed out:

```
=====
fragment pair information
=====
```

Numbers of the fragment pairs whose dimer calculations are performed with and without dimer-es approximation are printed out. Additionally, the information is also given with divided into the size of basis function.

3.7 Monomer SCC calculation

After the following keyword, progress of the monomer SCC calculations is printed out:

```
=====
monomer scc calculation ( dynamic update )
=====
```

3.7.1 < monomer scc cycle >

For each iteration, the FMO1–RHF energy and its difference, the maximum difference of monomer energy and its sequential number of fragment, and the computational times are printed out. Here, the FMO1–RHF energy is the following value (see the section 4.1):

$$\sum_I \left\{ E_I'^{HF} + \text{Tr}(\mathbf{D}_I^{HF} \mathbf{V}_I^{ext}) + E_I^Z + Z_I^{Zext} \right\}$$

3.8 Monomer SCC result

After the following keyword, results of the monomer SCC calculation are printed out:

```
=====
monomer scc result
=====
```

3.8.1 < monomer scc charge center >

[+ charge center] :

The center of the positive charge of each fragment. These values just depend on the coordinates of the nuclei.

[– charge center] :

The center of the negative charge of each fragment. These values depend on the electron density determined by the monomer SCC calculation.

3.9 Monomer calculation

After the following keyword, progress of each monomer calculation is printed out:

```
=====
[ A ] , monomer calculation : ifrag = [ B ]
=====
```

[A] and [B] is sequential sequential number of the monomer calculations and the fragments, respectively (monomer calculations are performed to order with large size). Note that only the monomer calculations performed with the core whose `mpi_rank` is 0 are printed out. For each monomer calculation, the progress of the calculations are printed out by the following order:

- monomer rhf
- monomer cmp2
- monomer ri-cmp2
- monomer lmp2
- monomer field property

3.10 FMO–1 result

After the following keyword, values evaluated using the monomer calculation results are printed out.

```
=====
fmo-1 result
=====
```

3.10.1 < monomer rhf energy >**[rhf(E'+ext)] :**

The monomer energy of each fragment including the nucleus potential and the interaction energy with the external potential. The contribution of the environmental electrostatic potential is excluded (see the sections 4.1.1 and 4.1.5).

$$E_I'^{HF} + Tr(\mathbf{D}_I^{HF} \mathbf{V}_I^{ext}) + E_I^Z + E_I^{Zext}$$

[rhf(E')] :

The value obtained by excluding the interaction energy with the external potential from the [rhf(E'+ext)]. Thus, in the case that the external potential dose not exist, this value is equivalent to the [rhf(E'+ext)] (see the sections 4.1.4).

$$E_I'^{HF} + E_I^Z$$

3.10.2 < monomer cmp2 corr. energy >**[cmp2(normal)] :**

The MP2 correlation energy of each monomer (see the sections 4.4.1).

$$E_I^{corr(MP2)}$$

[cmp2(grimme)] :

The SCS-MP2 correlation energy of each monomer with Grimme's factor (see the sections 4.4.1 and 4.4.3).

$$E_I^{corr(MP2-1)}$$

[cmp2(jung)] :

SCS-MP2 correlation energy of each monomer with Jung's factor (see the sections 4.4.1 and 4.4.3).

$$E_I^{corr(MP2-2)}$$

[cmp2(hill)] :

SCS-MP2 correlation energy of each monomer with Hill's factor (see the sections 4.4.1 and 4.4.3).

$$E_I^{corr(MP2-3)}$$

3.10.3 < monomer ri-cmp2 corr. energy >**[ri-cmp2(normal)] :**

The RI-MP2 correlation energy of each monomer (see the sections 4.5.1).

$$E_I^{corr(RI-MP2)}$$

3.10.4 < monomer lmp2 corr. energy >**[lmp2] :**

The LMP2 correlation energy of each monomer (see the sections 4.6.1).

$$E_I^{corr(LMP2)}$$

3.10.5 < rhf total energy (fmo-1) >

[total] :

FMO1 energy in the RHF calculation including the nucleus potential and the interaction energy with the external potential (see the sections 4.1.1 and 4.1.5).

$$\sum_I \left\{ E_I'^{HF} + Tr(\mathbf{D}_I^{HF} \mathbf{V}_I^{ext}) + E_I^Z + E_I^{Zext} \right\}$$

[internal] :

The value obtained by excluding the interaction energy with the external potential from the [total] . Thus, in the case that the external potential dose not exist, this value is equivalent to the [total] (see the sections 4.1.4 and 4.1.5).

$$\sum_I (E_I'^{HF} + E_I^Z)$$

[external] :

The contribution of the interaction energy with the external potential in the [total] . Thus, sum of the [internal] and [external] is equivalent to the [total] . In the case that the external potential dose not exist, this value is zero (see the sections 4.1.1 and 4.1.5).

$$\sum_I \left\{ Tr(\mathbf{D}_I^{HF} \mathbf{V}_I^{ext}) + E_I^{Zext} \right\}$$

3.10.6 < cmp2 total energy (fmo-1) >

[normal] :

MP2 correlatoin energy of the FMO1. Correlation energy and sum with the RHF energy are printed out (see the sections 4.4.1).

$$E_{fmo1}^{corr(MP2)}, E_{fmo1}^{HF(ext+Z)} + E_{fmo1}^{corr(MP2)}$$

[Grimm's scs] :

SCS-MP2 correlatoin energy of the FMO1 scaled with Grimme's factor. Correlation energy and sum with the RHF energy are printed out (see the sections 4.4.1 and 4.4.3).

$$E_{fmo1}^{corr(MP2-1)}, E_{fmo1}^{HF(ext+Z)} + E_{fmo1}^{corr(MP2-1)}$$

[Jung's scs] :

MP2 correlatoin energy of the FMO1 scaled with factors developed by Jung. Correlation energy and sum with the RHF energy are printed out (see the sections 4.4.1 and 4.4.3).

$$E_{fmo1}^{corr(MP2-1)}, E_{fmo1}^{HF(ext+Z)} + E_{fmo1}^{corr(MP2-2)}$$

[Hill's scs] :

MP2 correlatoin energy of the FMO1 scaled with factors developed by Hill. Correlation energy and sum with the RHF energy are printed out (see the sections 4.4.1 and 4.4.3).

$$E_{fmo1}^{corr(MP2-1)}, E_{fmo1}^{HF(ext+Z)} + E_{fmo1}^{corr(MP2-3)}$$

3.10.7 < ri-cmp2 total energy (fmo-1) >**[normal] :**

RI-MP2 correlatoin energy of the FMO1. Correlation energy and sum with the RHF energy are printed out (see the sections 4.5.1).

$$E_{fmo1}^{corr(RI-MP2)}, E_{fmo1}^{HF(ext+Z)} + E_{fmo1}^{corr(RI-MP2)}$$

3.10.8 < lmp2 total energy (fmo-1) >**[normal] :**

LMP2 correlatoin energy of the FMO1. Correlation energy and sum with the RHF energy are printed out (see the sections 4.6.1).

$$E_{fmo1}^{corr(LMP2)}, E_{fmo1}^{HF(ext+Z)} + E_{fmo1}^{corr(LMP2)}$$

3.11 Dimer-es approximation

After the following keyword, progress of the dimer-es approximation are printed out.

```
=====
dimer-es approximation : total pair = [ A ]
=====
```

3.11.1 < energy >

progress of dimer-es calculation (contribution to energy) is printed out.

3.11.2 < gradient >

progress of dimer-es calculation (contribution to gradient) is printed out.

3.12 Dimer calculations

After the following keyword, progress of each dimer calculation is printed out:

```
=====
[ A ] / [ b ], dimer calculation: ( ifrag, jfrag, dist ) = ( [ ], [ ], [ ] )
=====
```

where [A] and [B] are sequential serial numbers of the dimer calculations and the fragment pairs, respectively (dimer calculations are performed to order with large size). Note that only the dimer calculations performed with core whose `mpi_rank` is 0 are printed out. For each dimer calculation, the progress of the calculations are printed out by the following order:

- dimer rhf
- dimer cmp2
- dimer ri-cmp2
- dimer lmp2
- dimer field property

3.13 FMO-2 result

After the following keyword, values evaluated using the monomer and dimer calculations are printed out.

```
=====
fmo-2 result
=====
```

3.13.1 < rhf ifie >

[rhf] :

The IFIE including the nucleus potential and the interaction energy with the external potential (see the section 4.1.1 and 4.1.2).

$$\Delta E_{IJ}^{HF} + Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}^{ext}) + E_{IJ}^Z$$

[rhf (cp)] :

The value obtained by subtracting the estimated BSSE from the [rhf] (see the section 4.1.8).

$$\Delta E_{IJ}^{HF} + Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}^{ext}) + E_{IJ}^Z - E_{IJ}^{BSSE(HF)}$$

3.13.2 < cmp2 ifie >

[normal (not scs)] :

Contribution to the IFIE of the MP2 correlation. In the case performing the BSSE correction, the corrected value is additionally printed out (see the section 4.4.1 and 4.4.2).

$$\Delta E_{IJ}^{corr(MP2)}, \Delta E_{IJ}^{corr(MP2)} - E_{IJ}^{BSSE(corr(MP2))}$$

[Grimme's scs] :

Contribution to the IFIE of the SCS-MP2 correlation with Grimme's factor. In the case performing the BSSE correction, the corrected value is additionally printed out (see the section 4.4.3).

$$\Delta E_{IJ}^{corr(MP2-1)}, \Delta E_{IJ}^{corr(MP2-1)} - E_{IJ}^{BSSE(corr(MP2-1))}$$

[Jung's scs] :

Contribution to the IFIE of the SCS-MP2 correlation with Jung's factor. In the case performing the BSSE correction, the corrected value is additionally printed out (see the section 4.4.3).

$$\Delta E_{IJ}^{corr(MP2-2)}, \Delta E_{IJ}^{corr(MP2-2)} - E_{IJ}^{BSSE(corr(MP2-2))}$$

[Hill's scs] :

Contribution to the IFIE of the SCS-MP2 correlation with Hill's factor. In the case performing the BSSE correction, the corrected value is additionally printed out (see the section 4.4.3).

$$\Delta E_{IJ}^{corr(MP2-3)}, \Delta E_{IJ}^{corr(MP2-3)} - E_{IJ}^{BSSE(corr(MP2-3))}$$

3.13.3 < ri-cmp2 ifie >**[normal (not scs)] :**

Contribution to the IFIE of the RI-MP2 correlation. In the case performing the BSSE correction, the corrected value is additionally printed out (see the section 4.5.1 and 4.5.2).

$$\Delta E_{IJ}^{corr(RI-MP2)}, \quad \Delta E_{IJ}^{corr(RI-MP2)} - E_{IJ}^{BSSE(corr(RI-MP2))}$$

3.13.4 < lmp2 ifie >**[lmp2-ifie] :**

Contribution to the IFIE of the LMP2 correlation.

$$\Delta E_{IJ}^{corr(LMP2)(sum)} \quad (3.13.1)$$

3.13.5 < rhf total energy (fmo-2) >**[total] :**

FMO2 energy in the RHF calculation including the nucleus potential and the interaction energy with the external potential (see the section 4.5.3, texts4.1.6, and 4.1.7).

$$\begin{aligned} & \sum_I \left\{ E_I'^{HF} + Tr(\mathbf{D}_I^{HF} \mathbf{V}_I^{ext}) + E_I^Z + E_I^{Zext} \right\} \\ & + \sum_{I>J} \left\{ (E_{IJ}'^{HF} - E_I'^{HF} - E_J'^{HF}) \right. \\ & \quad \left. + Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}) + E_{IJ}^Z + Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}^{ext}) \right\} \end{aligned}$$

[internal] :

The value obtained by excluding the interaction energy with the external potential from the [total]. Thus, in the case that the external potential dose not exist, this value is equivalent to the [total] (see the section 4.5.3, texts4.1.6, and 4.1.7).

$$\sum_I (E_I'^{HF} + E_I^Z) + \sum_{I>J} \left\{ (E_{IJ}'^{HF} - E_I'^{HF} - E_J'^{HF}) + Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}) + E_{IJ}^Z \right\}$$

[external] :

Only the contribution of the interaction energy with the external potential in the [total]. Thus, sum of the [internal] and [external] is equivalent to the [total]. In the case that the external potential dose not exist, this value is zero (see the section 4.5.3, texts4.1.6, and 4.1.7).

$$\sum_I \left\{ Tr(\mathbf{D}_I^{HF} \mathbf{V}_I^{ext}) + E_I^{Zext} \right\} + \sum_{I>J} Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}^{ext})$$

3.13.6 < cmp2 total energy (fmo-2) >**[normal] :**

MP2 correlatoin energy of the FMO2. Correlation energy and sum with the RHF energy are printed out (see the section 4.4.1).

$$E_{fmo2}^{corr(MP2)}, \quad E_{fmo2}^{HF(ext+Z)} + E_{fmo2}^{corr(MP2)}$$

[Grimm's scs] :

MP2 correlatoin energy of the FMO2 scaled with factors developed by Grimme. Correlation energy and sum with the RHF energy are printed out (see the section 4.4.3).

$$E_{fmo2}^{corr(MP2-1)}, E_{fmo2}^{HF(ext+Z)} + E_{fmo2}^{corr(MP2-1)}$$

[Jung's scs] :

MP2 correlatoin energy of the FMO2 scaled with factors developed by Jung. Correlation energy and sum with the RHF energy are printed out (see the section 4.4.3).

$$E_{fmo2}^{corr(MP2-2)}, E_{fmo2}^{HF(ext+Z)} + E_{fmo2}^{corr(MP2-2)}$$

[Hill's scs] :

MP2 correlatoin energy of the FMO2 scaled with factors developed by Hill. Correlation energy and sum with the RHF energy are printed out (see the section 4.4.3).

$$E_{fmo2}^{corr(MP2-3)}, E_{fmo2}^{HF(ext+Z)} + E_{fmo2}^{corr(MP2-3)}$$

3.13.7 < ri-cmp2 total energy (fmo-2) >**[normal] :**

RI-MP2 correlatoin energy of the FMO2. Correlation energy and sum with the RHF energy are printed out (see the section 4.5.1).

$$E_{fmo2}^{corr(RI-MP2)}, E_{fmo2}^{HF(ext+Z)} + E_{fmo2}^{corr(RI-MP2)}$$

3.13.8 < lmp2 total energy (fmo-2) >**[sub.]**

LMP2 correlatoin energy of the FMO2. Correlation energy and sum with the RHF energy are printed out

$$E_{fmo2}^{corr(LMP2)}, E_{fmo2}^{HF(ext+Z)} + E_{fmo2}^{corr(LMP2)}$$

[sum.]

LMP2 correlatoin energy of the FMO2. Correlation energy and sum with the RHF energy are printed out

$$E_{fmo2}^{corr(LMP2)(sum)}, E_{fmo2}^{HF(ext+Z)} + E_{fmo2}^{corr(LMP2)(sum)}$$

3.13.9 < rhf mulliken population (fmo-2) >**[pop.] :**

Mulliken population of the electron density of the FMO2-RHF.

$$N_{fmo2}^{HF}(A)$$

[charge] :

Sum of the [pop.] and nucleus charge.

$$-N_{fmo2}^{HF}(A) + Z_A$$

3.13.10 < cmp2 mulliken population (fmo-2) >**[pop.] :**

Mulliken population of the electron density of the FMO2-MP2.

$$N_{fmo2}^{MP2}(A)$$

[charge] :

Sum of the [pop.] and nucleus charge.

$$-N_{fmo2}^{MP2}(A) + Z_A$$

[cmp2-corr.] :

Correction by the MP2 correlation.

$$N_{fmo2}^{corr(MP2)}(A)$$

3.13.11 < ri-cmp2 mulliken population (fmo-2) >**[pop.] :**

Mulliken population of the electron density of the FMO2-RI-MP2.

$$N_{fmo2}^{RI-MP2}(A)$$

[charge] :

Sum of the [pop.] and nucleus charge.

$$-N_{fmo2}^{RI-MP2}(A) + Z_A$$

[cmp2-corr.] :

Correction by the MP2 correlation.

$$N_{fmo2}^{corr(RI-MP2)}(A)$$

3.13.12 < rhf gradient (fmo-2 , hartree/hohr) >**[x , y , z] :**

Values of x, y, and z-component of the FMO2-RHF gradient of each atom (see section 4.2.2, 4.2.5, 4.2.6). This value includes the terms of the external electrostatic potential (Eq. 4.2.40) and nucleus potential (Eq. 4.2.41).

$$\begin{aligned} \frac{\partial}{\partial A} E_{fmo2}^{HF} + \frac{\partial}{\partial A} \left(\sum_I E_I^{ZZ} + \sum_{I<J} E_{IJ}^{ZZ} + \sum_I E_I^{Zext} \right) \\ - (N_f - 2) \sum_I \sum_{\mu\nu \in I} D_{I\mu\nu}^{HF} \frac{\partial}{\partial A} V_{I\mu\nu}^{ext} + \sum_{I<J} \sum_{\mu\nu \in IJ} D_{IJ\mu\nu}^{HF} \frac{\partial}{\partial A} V_{IJ\mu\nu}^{ext} \end{aligned} \quad (3.13.2)$$

3.13.13 < cmp2 gradient (fmo-2 , hartree/hohr) >**[x , y , z] :**

Values of x, y, and z-component of the FMO2-MP2 gradient of each atom. Sum with the FMO2-RHF gradient is printed out together with the correlation contribution. This the correlation contribution includes the terms of the external electrostatic potential.

$$\frac{\partial}{\partial A} E_{fmo2}^{HF(ext+Z)} + \frac{\partial}{\partial A} E_{fmo2}^{corr(MP2)} \quad (3.13.3)$$

[cmp2-corr.] :

$$\frac{\partial}{\partial A} E_{fmo2}^{corr(MP2)} \quad (3.13.4)$$

3.13.14 < ri-cmp2 gradient (fmo-2 , hartree/hohr) >

[x , y , z] :

Values of x, y, and z-component of the FMO2-RI-MP2 gradient of each atom. Sum with the FMO2-RHF gradient is printed out together with the correlation contribution. This the correlation contribution includes the terms of the external electrostatic potential.

$$\frac{\partial}{\partial A} E_{fmo2}^{HF(ext+Z)} + \frac{\partial}{\partial A} E_{fmo2}^{corr(RI-MP2)} \quad (3.13.5)$$

[ri-cmp2-corr.] :

$$\frac{\partial}{\partial A} E_{fmo2}^{corr(RI-MP2)} \quad (3.13.6)$$

3.13.15 < rhf electron density (fmo-2) >

[density] :

Electron density of the FMO2-RHF at the positions defined by the input.

$$\rho_{fmo2}^{HF}(\mathbf{r}_m)$$

3.13.16 < cmp2 electron density (fmo-2) >

[density] :

Electron density of the FMO2-MP2 at the positions defined by the input.

$$\rho_{fmo2}^{MP2}(\mathbf{r}_m)$$

[cmp2-corr.] :

$$\rho_{fmo2}^{corr(MP2)}(\mathbf{r}_m)$$

3.13.17 < ri-cmp2 electron density (fmo-2) >

[density] :

Electron density of the FMO2-RI-MP2 at the positions defined by the input.

$$\rho_{fmo2}^{RI-MP2}(\mathbf{r}_m)$$

[ri-cmp2-corr.] :

$$\rho_{fmo2}^{corr(RI-MP2)}(\mathbf{r}_m)$$

3.13.18 < rhf electrostatic potential (fmo-2) >**[esp (elec.)] :**

Electrostatic potential by the electron density of the FMO2-RHF at the positions defined by the input.

$$\phi_{fmo2}^{HF}(\mathbf{r}_m)$$

[esp (nuc.)] :

Electrostatic potential by the nucleus charge at the positions defined by the input. In the case that the calculated position is exactly overlapped to the nucleus position, the contribution of this nucleus is excluded ("*" is attached).

[esp (sum)] :

The sum of the [esp (elec.)] and [esp (nuc.)]. The contribution of the external potential is not included.

3.13.19 < cmp2 electrosatic potential (fmo-2) >**[esp (elec.)] :**

Electrostatic potential by the electron density of the FMO2-MP2 at the positions defined by the input.

$$\phi_{fmo2}^{MP2}(\mathbf{r}_m)$$

[esp (nuc.)] :

Electrostatic potential by the nucleus charge at the positions defined by the input. In the case that the calculated position is exactly overlapped to the nucleus position, the contribution of this nucleus is excluded ("*" is attached).

[esp (sum)] :

The sum of the [esp (elec.)] and [esp (nuc.)]. The contribution of the external potential is not included.

[cmp2-corr.] :

$$\phi_{fmo2}^{corr(MP2)}(\mathbf{r}_m) \tag{3.13.7}$$

3.13.20 < ri-cmp2 electrstatic potential (fmo-2) >**[esp (elec.)] :**

Electrostatic potential by the electron density of the FMO2-RI-MP2 at the positions defined by the input.

$$\phi_{fmo2}^{RI-MP2}(\mathbf{r}_m)$$

[esp (nuc.)] :

Electrostatic potential by the nucleus charge at the positions defined by the input. In the case that the calculated position is exactly overlapped to the nucleus position, the contribution of this nucleus is excluded ("*" is attached).

[esp (sum)] :

The sum of the [esp (elec.)] and [esp (nuc.)]. The contribution of the external potential is not included.

[ri-cmp2-corr.] :

$$\phi_{fmo2}^{corr(RI-MP2)}(\mathbf{r}_m) \quad (3.13.8)$$

3.13.21 < rhf electric field (fmo-2) >

[(ele)] :

Electric field by the electron density of the FMO2-RHF at the positions defined by the input.

$$\mathbf{E}_{fmo2}^{HF}(\mathbf{r}_m)$$

[(nuc)] :

Electric field by the nucleus charge at the positions defined by the input. In the case that the calculated position is exactly overlapped to the nucleus position, the contribution of this nucleus is excluded ("*" is attached).

[(sum)] :

The sum of the [(elec)] and [(nuc)]. The contribution of the external potential is not included.

3.13.22 < cmp2 electric field (fmo-2) >

[(ele)] :

Electric field by the electron density of the FMO2-MP2 at the positions defined by the input.

$$\mathbf{E}_{fmo2}^{MP2}(\mathbf{r}_m)$$

[(nuc)] :

Electric field by the nucleus charge at the positions defined by the input. In the case that the calculated position is exactly overlapped to the nucleus position, the contribution of this nucleus is excluded ("*" is attached).

[(sum)] :

The sum of the [(elec)] and [(nuc)]. The contribution of the external potential is not included.

3.13.23 < ri-cmp2 electric field (fmo-2) >

[(ele)] :

Electric field by the electron density of the FMO2-RI-MP2 at the positions defined by the input.

$$\mathbf{E}_{fmo2}^{RI-MP2}(\mathbf{r}_m)$$

[(nuc)] :

Electric field by the nucleus charge at the positions defined by the input. In the case that the calculated position is exactly overlapped to the nucleus position, the contribution of this nucleus is excluded ("*" is attached).

[(sum)] :

The sum of the [(elec)] and [(nuc)]. The contribution of the external potential is not included.

Chapter 4

Theory

4.1 FMO–RHF (energy)

In this section, the theory related to the calculation of the FMO–RHF energy is explained, making it be related to the output of the *PAICS*. The formulation basically follows the previous publications reporting the theory and method of the FMO scheme [1, 2, 3, 4, 5, 6, 7].

4.1.1 Definition of operators

In the FMO method, a target molecule is divided into small fragments, and only calculations of the fragments (referred to as monomer) and pairs of the fragments (referred to as dimer) are performed. The total energy could be evaluated using the results of monomer and dimer calculations. In these calculations, the modified Fock operator is used, which is

$$f_X = \tilde{f}_X + \sum_{K \neq X} \left(u_{X(K)} + v_{X(K)} \right) + P_X, \quad (4.1.1)$$

where X is index of the fragment or pair of fragments, i.e., X is replaced by I and IJ for monomer and dimer calculations, respectively. The first term of this operator is a normal Fock operator:

$$\tilde{f}_X = h_X + 2 J_X - K_X, \quad (4.1.2)$$

where h_X is one electron operator:

$$h_X = -\frac{1}{2} \nabla^2 + \sum_{A \in X} \frac{-Z_A}{|\mathbf{R}_A - \mathbf{r}_1|}, \quad (4.1.3)$$

and J^X and K^X are coulomb and exchange operators, respectively. The second term of the Eq. 4.1.1 is electrostatic potentials from the other fragments, which are defined as

$$u_{X(K)} = \sum_{A \in K} \frac{-Z_A}{|\mathbf{R}_A - \mathbf{r}_1|}, \quad (4.1.4)$$

$$v_{X(K)} = \int d\mathbf{r}_2 \frac{\rho^K(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|}, \quad (4.1.5)$$

where $u_{X(K)}$ is attractive potential of X from the nuclei of the K -th fragment, and $v_{X(K)}$ is repulsive potential of X from the electron density of the K -th fragment. The electron density of each fragment is determined with an iterative procedure called "monomer self consistent charge (SCC) calculation", and potential from the other fragment is called "environmental electrostatic potential". The third term is the projection operator related to cut of covalent bonds in the fragmentation:

$$P_X = B \sum_k |\theta_X^k\rangle\langle\theta_X^k| \quad (4.1.6)$$

where θ_X^k is a component excluded from the variational space of the monomer and dimer calculations, and B is a sufficiently large positive value.

4.1.2 Definition of matrixes

Here, we define the several matrices associated with above operator:

$$h_{X\mu\nu} = \langle\mu|h_X|\nu\rangle, \quad (4.1.7)$$

$$u_{X(K)\mu\nu} = \langle\mu|u_{X(K)}|\nu\rangle, \quad (4.1.8)$$

$$v_{X(K)\mu\nu} = \langle\mu|v_{X(K)}|\nu\rangle, \quad (4.1.9)$$

$$P_{X\mu\nu} = \langle\mu|P_X|\nu\rangle, \quad (4.1.10)$$

$$J_{X\mu\nu} = \langle\mu|J_X|\nu\rangle, \quad (4.1.11)$$

$$K_{X\mu\nu} = \langle\mu|K_X|\nu\rangle, \quad (4.1.12)$$

where $\mu, \nu, \lambda, \sigma, \dots$ are indices of the basis functions of X . Using these matrices, we introduce the other matrices:

$$\mathbf{V}_{X(K)} = \mathbf{u}_{X(K)} + \mathbf{v}_{X(K)}, \quad (4.1.13)$$

$$\mathbf{V}_X = \sum_{K \neq X} \mathbf{V}_{X(K)}, \quad (4.1.14)$$

$$\tilde{\mathbf{h}}_X = \mathbf{h}_X + \mathbf{V}_X + \mathbf{P}_X, \quad (4.1.15)$$

$$\tilde{\mathbf{F}}_X = \tilde{\mathbf{h}}_X + 2\mathbf{J}_X - \mathbf{K}_X. \quad (4.1.16)$$

The molecular orbitals determined by the Fock equation with the operator of Eq. 4.1.1 are defined as

$$\psi_{X,i}^{HF} = \sum_{\mu} \mu(\mathbf{r}) C_{X,\mu i}^{HF}, \quad (4.1.17)$$

and the density matrix is defined as

$$D_{X,\mu\nu}^{HF} = 2 \sum_i C_{X,\mu i}^{HF} C_{X,\nu i}^{HF}. \quad (4.1.18)$$

4.1.3 Energy

The HF energies of the monomer and dimer are

$$E_X^{HF} = \frac{1}{2} \text{Tr} \left\{ \mathbf{D}_X^{HF} (\tilde{\mathbf{h}}_X + \tilde{\mathbf{F}}_X) \right\}. \quad (4.1.19)$$

Here, we introduce a new energy which is obtained by excluding the contribution of the environmental electrostatic potential from the E_X^{HF} , that is,

$$E'_X{}^{HF} = E_X^{HF} - \text{Tr}(\mathbf{D}_X^{HF} \mathbf{V}_X). \quad (4.1.20)$$

The total energy of the one-body approximation of the FMO method (FMO1) is defined as

$$E_{fmo1}^{HF} = \sum_I E'_I{}^{HF}, \quad (4.1.21)$$

and the total energy of the two-body approximation of the FMO method (FMO2) is defined as

$$E_{fmo2}^{HF} = \sum_{I < J} E_{IJ}^{HF} - (N_f - 2) \sum_I E_I^{HF}. \quad (4.1.22)$$

This FMO2 energy can be written as

$$E_{fmo2}^{HF} = \sum_I E_I^{HF} + \sum_{I > J} (E_{IJ}^{HF} - E_I^{HF} - E_J^{HF}). \quad (4.1.23)$$

Here, we introduce a new matrix $\mathbf{D}^{I(J)}$, whose dimension is same as that of the density matrix of dimer IJ , and the matrix elements are defined as

$$\begin{aligned} \mu \in I \text{ and } \nu \in I & \quad D_{I(J) \mu\nu}^{HF} = D_I^{HF}{}_{\mu\nu}, \\ \text{the others} & \quad D_{I(J) \mu\nu}^{HF} = 0. \end{aligned}$$

Using this matrix, the FMO2-RHF energy is written as

$$\begin{aligned} E_{fmo2}^{HF} = & \sum_I E'_I{}^{HF} + \sum_{I > J} (E'_{IJ}{}^{HF} - E'_I{}^{HF} - E'_J{}^{HF}) \\ & + \sum_{I > J} \left\{ \text{Tr}(\mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}) - \text{Tr}(\mathbf{D}_{I(J)}^{HF} \mathbf{V}_{IJ}) - \text{Tr}(\mathbf{D}_{J(I)}^{HF} \mathbf{V}_{IJ}) \right\}. \end{aligned} \quad (4.1.24)$$

Additionally, we introduce a new matrix

$$\Delta \mathbf{D}_{IJ}^{HF} = \mathbf{D}_{IJ}^{HF} - \mathbf{D}_{I(J)}^{HF} - \mathbf{D}_{J(I)}^{HF}. \quad (4.1.25)$$

Using this matrix, the FMO2-RHF energy is written as

$$E_{fmo2}^{HF} = \sum_I E'_I{}^{HF} + \sum_{I > J} (E'_{IJ}{}^{HF} - E'_I{}^{HF} - E'_J{}^{HF}) + \sum_{I > J} \text{Tr}(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}^{HF}). \quad (4.1.26)$$

Here, we introduce a new value

$$\Delta E_{IJ}^{HF} = (E'_{IJ}{}^{HF} - E'_I{}^{HF} - E'_J{}^{HF}) + \text{Tr}(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}^{HF}), \quad (4.1.27)$$

and using this value, the FMO2-RHF energy is written as the following equation:

$$E_{fmo2}^{HF} = E_{fmo1}^{HF} + \sum_{I > J} \Delta E_{IJ}^{HF}. \quad (4.1.28)$$

Thus, we can consider that the second term of this equation is the two-body correction on the FMO1-RHF energy, and which is called inter fragment interaction energy (IFIE) or pair interaction energy (PIE).

4.1.4 Dimer-es approximation

For the dimers constructed with largely separated fragments, the E'^{HF}_{IJ} is approximately calculated by considering only the electrostatic interaction between the two fragments. This treatment is called "dimer-es approximation". In this approximation, the E'^{HF}_{IJ} is evaluated as the following equation:

$$E'^{HF}_{IJ} = E'^{HF}_I + E'^{HF}_J + \sum_{A \in J} \int \frac{-Z_A \rho_I(\mathbf{r}_1)}{|\mathbf{R}_A - \mathbf{r}_1|} d\mathbf{r}_1 + \sum_{A \in I} \int \frac{-Z_A \rho_J(\mathbf{r}_1)}{|\mathbf{R}_A - \mathbf{r}_1|} d\mathbf{r}_1 + \int \frac{\rho_I(\mathbf{r}_1) \rho_J(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} d\mathbf{r}_1 d\mathbf{r}_2. \quad (4.1.29)$$

This equation can be written with the density matrices as

$$E'^{HF}_{IJ} = E'^{HF}_I + E'^{HF}_J + \sum_{\mu\nu \in I} D_{I\mu\nu}^{HF} u_{I(J)\mu\nu} + \sum_{\mu\nu \in J} D_{J\mu\nu}^{HF} u_{J(I)\mu\nu} + \sum_{\mu\nu \in I} \sum_{\lambda\sigma \in J} D_{I\mu\nu}^{HF} D_{J\lambda\sigma}^{HF} (\mu\nu | \lambda\sigma). \quad (4.1.30)$$

Additionally, for the dimer-es pairs, the following equation is satisfied:

$$Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}) = Tr(\mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}) - Tr(\mathbf{D}_{I(I)}^{HF} \mathbf{V}_{IJ}) - Tr(\mathbf{D}_{J(I)}^{HF} \mathbf{V}_{IJ}) = 0. \quad (4.1.31)$$

Thus, by combining this equation with Eq. (4.1.27), the ΔE_{IJ}^{HF} is approximately written as

$$\Delta E_{IJ}^{HF} = E'^{HF}_{IJ} - E'^{HF}_I - E'^{HF}_J. \quad (4.1.32)$$

Consequently, by substituting Eq. (4.1.30) to Eq. (4.1.32), we obtain the following equation:

$$\begin{aligned} \Delta E_{IJ}^{HF} = & \sum_{\mu\nu \in I} D_{I\mu\nu}^{HF} u_{I(J)\mu\nu} + \sum_{\mu\nu \in J} D_{J\mu\nu}^{HF} u_{J(I)\mu\nu} \\ & + \sum_{\mu\nu \in I} \sum_{\lambda\sigma \in J} D_{I\mu\nu}^{HF} D_{J\lambda\sigma}^{HF} (\mu\nu | \lambda\sigma). \end{aligned} \quad (4.1.33)$$

This is the IFIE for the dimer-es pairs.

4.1.5 Environmental electrostatic potential

The matrix of the environmental electrostatic potential ($\mathbf{V}_X$) is written as sum of the attractive potential and repulsive potential from the other fragments, i.e.,

$$\mathbf{V}_X = \sum_{K \neq X} \mathbf{u}_{X(K)} + \sum_{K \neq X} \mathbf{v}_{X(K)}, \quad (4.1.34)$$

where the first term of this equation is calculated as

$$\sum_{K \neq X} u_{X(K)\mu\nu} = \langle \mu | \sum_{K \neq X} \sum_{A \in K} \frac{-Z_A}{|\mathbf{R}_A - \mathbf{r}_1|} | \nu \rangle. \quad (4.1.35)$$

On the other hands, the second term of this equation is evaluated using three types of manner:

1. evaluated without any approximation, i.e., 4-center electron repulsion integrals are used.
2. approximately evaluated with 3-center integrals, which is called "**esp-aoc**" approximation.
3. approximately evaluated with point charges, which is called "**esp-ptc**" approximation.

Here, we write the potential from the electron density in the form of the summation over the contributions of the three types of manner as the following equation:

$$\sum_{K \neq X} \mathbf{v}_{X(K)} = \sum_{K_4} \mathbf{v}_{X(K_4)}^4 + \sum_{K_3} \mathbf{v}_{X(K_3)}^3 + \sum_{K_p} \mathbf{v}_{X(K_p)}^p, \quad (4.1.36)$$

where K_4 , K_3 , and K_p indicate the fragments, whose potential are evaluated with 4-center integrals, 3-center integrals, and point charges, respectively.

< evaluation of the electrostatic potential with 4-center integrals >

The first term of Eq. (4.1.36) is evaluated from the electron density of the K_4 -th fragment:

$$\sum_{K_4} v_{X(K_4)\mu\nu}^4 = \sum_{K_4} \langle \mu | \int d\mathbf{r}_2 \frac{\rho_{K_4}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} | \nu \rangle. \quad (4.1.37)$$

where the $\rho^{K_4}(\mathbf{r})$ is evaluated with the density matrix of the K_4 -th fragment determined by the monomer SCC calculation, that is,

$$\rho_{K_4}(\mathbf{r}) = \sum_{\lambda\sigma \in K_4} D_{K_4}^{HF}{}_{\lambda\sigma} \lambda(\mathbf{r})\sigma(\mathbf{r}). \quad (4.1.38)$$

Thus, the first term of Eq. (4.1.36) can be written with the 4-center integrals as the following equation:

$$\sum_{K_4} v_{X(K_4)\mu\nu}^4 = \sum_{K_4} \sum_{\lambda\sigma \in K_4} D_{K_4}^{HF}{}_{\lambda\sigma} (\mu\nu | \lambda\sigma). \quad (4.1.39)$$

< evaluation of the electrostatic potential with 3-center integrals >

The second term of Eq. (4.1.36) is evaluated from the electron density of the K_3 -th fragment:

$$\sum_{K_3} v_{X(K_3)\mu\nu}^3 = \sum_{K_3} \langle \mu | \int d\mathbf{r}_2 \frac{\rho_{K_3}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} | \nu \rangle \quad (4.1.40)$$

where $\rho^{K_3}(\mathbf{r})$ is approximately evaluated with the density matrix of the K_3 -th fragment determined by the monomer SCC calculation, that is,

$$\rho_{K_3}(\mathbf{r}) = \sum_{\lambda \in K_3} \left(\sum_{\sigma \in K_3} D_{K_3}^{HF}{}_{\lambda\sigma} S_{K_3\sigma\lambda} \right) \lambda(\mathbf{r}) \lambda(\mathbf{r}) \quad (4.1.41)$$

Thus, the second term of Eq. (4.1.36) is written with the 3-center integrals as the following equation:

$$\sum_{K_3} v_{X(K_3)\mu\nu}^3 = \sum_{K_3} \sum_{\lambda \in K_3} (\mathbf{D}_{K_3}^{HF} \mathbf{S}_{K_3})_{\lambda\lambda} (\mu\nu | \lambda\lambda) \quad (4.1.42)$$

[caution]

In the program, Eq. (4.1.42) is calculated with the normalization factor as

$$\sum_{K_3} v_{X(K_3)\mu\nu}^3 = \sum_{K_3} \sum_{\lambda \in K_3} (\mathbf{D}_{K_3}^{HF} \mathbf{S}_{K_3})_{\lambda\lambda} \frac{1}{\langle \lambda | \lambda \rangle} (\mu\nu | \lambda\lambda). \quad (4.1.43)$$

< evaluation of the electrostatic potential with point charges >

The third term of Eq. (4.1.36) is evaluated from the electron density of the K_p -th fragments:

$$\sum_{K_p} v_{X(K_p)\mu\nu}^p = \sum_{K_p} \langle \mu | \int d\mathbf{r}_2 \frac{\rho_{K_p}(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} | \nu \rangle \quad (4.1.44)$$

where $\rho_{K_p}(\mathbf{r})$ is approximately treated as the point charges determined by the monomer SCC calculation. Thus, the third term of Eq. (4.1.36) is written with the point charge as the following equation:

$$\sum_{K_p} v_{X(K_p)\mu\nu}^p = \sum_{K_p} \langle \mu | \sum_{B \in K_p} \frac{q_B}{|\mathbf{R}_B - \mathbf{r}_1|} | \nu \rangle \quad (4.1.45)$$

4.1.6 Energy including external potential

In the case that the external potential exists, the Fock operator of Eq. (4.1.1) is modified as

$$f_X^{(ext)} = \tilde{f}_X + \sum_{K \neq X} (u_{X(K)} + v_{X(K)}) + P_X + V_X^{ext}, \quad (4.1.46)$$

where the last term is the operator associated with the external potential. Here, we define the matrix of the external potential as

$$V_{X\mu\nu}^{ext} = \langle \mu | V_X^{ext} | \nu \rangle. \quad (4.1.47)$$

In this case, contribution of the external potential is added to the $E'_X{}^{HF}$.

$$E'_X{}^{HF} \rightarrow E'_X{}^{HF} + Tr(\mathbf{D}_X^{HF} \mathbf{V}_X^{ext}). \quad (4.1.48)$$

Thus, the FMO1 energy is written as

$$E_{fmo1}^{HF(ext)} = \sum_I E'_I{}^{HF} + \sum_I Tr(\mathbf{D}_I^{HF} \mathbf{V}_I^{ext}). \quad (4.1.49)$$

With considering Eq. (4.1.26), the FMO2-RHF energy is written as

$$\begin{aligned} E_{fmo2}^{HF(ext)} &= \sum_I E'_I{}^{HF} + \sum_{I>J} (E'_{IJ}{}^{HF} - E'_I{}^{HF} - E'_J{}^{HF}) + \sum_{I>J} Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}) \\ &+ \sum_I Tr(\mathbf{D}_I^{HF} \mathbf{V}_I^{ext}) + \sum_{I>J} \left\{ Tr(\mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}^{ext}) - Tr(\mathbf{D}_I^{HF} \mathbf{V}_I^{ext}) - Tr(\mathbf{D}_J^{HF} \mathbf{V}_J^{ext}) \right\}. \end{aligned} \quad (4.1.50)$$

For the matrix of the external potential, the following equations are satisfied:

$$Tr(\mathbf{D}_I^{HF} \mathbf{V}_I^{ext}) = Tr(\mathbf{D}_{I(J)}^{HF} \mathbf{V}_{IJ}^{ext}), \quad (4.1.51)$$

Thus, we can obtain the FMO2-RHF energy as

$$\begin{aligned} E_{fmo2}^{HF(ext)} &= \sum_I E'_I{}^{HF} + \sum_{I>J} (E'_{IJ}{}^{HF} - E'_I{}^{HF} - E'_J{}^{HF}) + \sum_{I>J} Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}) \\ &+ \sum_I Tr(\mathbf{D}_I^{HF} \mathbf{V}_I^{ext}) + \sum_{I>J} Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}^{ext}), \end{aligned} \quad (4.1.52)$$

and this equation is written using the FMO1-RHF energy as

$$E_{fmo2}^{HF(ext)} = E_{fmo1}^{HF(ext)} + \sum_{I>J} \left\{ (E'_{IJ}{}^{HF} - E'_I{}^{HF} - E'_J{}^{HF}) + Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}) + Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}^{ext}) \right\}. \quad (4.1.53)$$

The second term of this equation is the two-body correction on the FMO1 energy. Thus, we can define the IFIE including the external potential as the following equation:

$$\Delta E_{IJ}^{HF(ext)} = (E'_{IJ}{}^{HF} - E'_I{}^{HF} - E'_J{}^{HF}) + Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}) + Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}^{ext}) \quad (4.1.54)$$

4.1.7 Energy including nucleus potential

The monomer or dimer HF energy including the external electrostatic potential and nucleus potential ($E_X^{HF(ext+Z)}$) is written as:

$$E_X^{HF(ext+Z)} = E_X^{HF} + Tr(\mathbf{D}_X^{HF} \mathbf{V}_X^{ext}) + E_X^Z, \quad (4.1.55)$$

$$E_X^Z = \sum_{(A<B) \in X} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|} + \sum_{K \neq X} \sum_{A \in X} \sum_{C \in K} \frac{Z_A Z_C}{|\mathbf{R}_A - \mathbf{R}_C|} - \sum_{K \neq X} \sum_{A \in X} \int \frac{Z_A \rho_K(\mathbf{r})}{|\mathbf{R}_A - \mathbf{r}|} d\mathbf{r} + E_X^{Zext}, \quad (4.1.56)$$

where E_X^{Zext} is the interaction energy between the nuclei and external potential. The first term is the repulsive potential among the nuclei in X , and the second term is the repulsive potential between the nuclei in X and the K -th fragment. The third term is the attractive potential between the nucleus in X and the electron density of the K -th fragment. Here, we introduce some values defined as the following equations:

$$E_X^{ZZ} = \sum_{(A<B) \in X} \frac{Z_A Z_B}{|\mathbf{R}_A - \mathbf{R}_B|}, \quad (4.1.57)$$

$$E_{X(K)}^{ZZ} = \sum_{A \in X} \sum_{C \in K} \frac{Z_A Z_C}{|\mathbf{R}_A - \mathbf{R}_C|}, \quad (4.1.58)$$

$$E_{X(K)}^{Ze} = - \sum_{A \in X} \int \frac{Z_A \rho_K(\mathbf{r})}{|\mathbf{R}_A - \mathbf{r}|} d\mathbf{r}. \quad (4.1.59)$$

Using these values, Eq. (4.1.56) is written as

$$E_X^{HF(ext+Z)} = E_X^{HF} + Tr(\mathbf{D}_X^{HF} \mathbf{V}_X^{ext}) + E_X^{ZZ} + \sum_{K \neq X} E_{X(K)}^{ZZ} + \sum_{K \neq X} E_{X(K)}^{Ze} + E_X^{Zext}. \quad (4.1.60)$$

The FMO1-RHF energy is defined by excluding the contribution of the other fragments from sum of the monomer energies. Thus, the FMO1 energy including the nucleus potential is written as

$$E_{fmo1}^{HF(ext+Z)} = \sum_I E'_I{}^{HF} + Tr(\mathbf{D}_X^{HF} \mathbf{V}_X^{ext}) + \sum_I E_I^{ZZ} + \sum_I E_X^{Zext}. \quad (4.1.61)$$

The FMO2 energy is defined as

$$E_{fmo2}^{HF(ext+Z)} = \sum_{I < J} E_{IJ}^{HF(ext+Z)} - (N_f - 2) \sum_I E_I^{HF(ext+Z)}. \quad (4.1.62)$$

Thus, we can obtain the FMO2-RHF energy including the nucleus potential as

$$\begin{aligned} E_{fmo2}^{HF(ext+Z)} = E_{fmo2}^{HF} &+ \sum_I Tr(\mathbf{D}_I^{HF} \mathbf{V}_I^{ext}) + \sum_{I > J} Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}^{ext}) \\ &+ \sum_I E_I^{ZZ} + \sum_{I < J} E_{I(J)}^{ZZ} + \sum_I E_I^{Zext}, \end{aligned} \quad (4.1.63)$$

This is rewritten as

$$E_{fmo2}^{HF(ext+Z)} = E_{fmo1}^{HF(ext+Z)} + \sum_{I < J} \left(\Delta E_{IJ}^{HF} + Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}^{ext}) + E_{I(J)}^{ZZ} \right). \quad (4.1.64)$$

where the second term is two-body correction on the FMO1-RHF energy. Thus, we can consider that the second term of this equation is the IFIE explicitly including the nucleus potential, i.e.,

$$\Delta E_{IJ}^{HF(ext+Z)} = \Delta E_{IJ}^{HF} + Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}^{ext}) + E_{I(J)}^{ZZ}. \quad (4.1.65)$$

4.1.8 Restriction of dimer calculation

First, we divide the fragments into two groups (F_1 and F_2), and the fragments in the F_1 and F_2 are identified using the indices of IJ and KL , respectively. Using these indices, the FMO1-RHF energy in Eq. (4.1.21) is written as

$$E_{fmo1}^{HF} = \sum_I E_I'^{HF} + \sum_K E_K'^{HF}. \quad (4.1.66)$$

On the other hands, the FMO2-RHF energy in Eq. (4.1.28) is written as

$$\begin{aligned} E_{fmo2}^{HF} = \sum_I E_I'^{HF} &+ \sum_{I > J} \Delta E_{IJ}^{HF} + \sum_I \sum_K \Delta E_{IK}^{HF} \\ &+ \sum_K E_K'^{HF} + \sum_{K > L} \Delta E_{KL}^{HF} \end{aligned} \quad (4.1.67)$$

Here, we perform only the dimer calculations of the pair including the fragments in the F_1 . In this case, because the fifth term of Eq. (4.1.23) is not performed, the FMO2-RHF energy can not be calculated. But, at the following condition:

the number of fragments in $F_1 \ll$ the number of fragments in F_2 ,

much computational time can be reduces, because the majority of the dimer calculation is those of the fifth term. Thus, this restriction is useful for the case that only the interaction energies related to the fragment of F_1 are required. For example, in the case that the interaction of a ligand molecule with a protein is examined. In the **PAICS**, such a restricted calculations are performed with the `frag_calc_pair` keyword.

< definition of the partial energy >

The first and second terms in Eq. (4.1.67) give the internal energy of the fragments of F_1 , and the third term give the interaction energy between the fragments of F_1 and F_2 . Thus, we define the "partial energy" of F_1 as the following equation:

$$E_{fmo2(F_1)}^{HF} = \sum_I E_I'^{HF} + \sum_{I > J} \Delta E_{IJ}^{HF} + \sum_I \sum_K \Delta E_{IK}^{HF}. \quad (4.1.68)$$

This is used for the definition of the partial energy gradient.

4.1.9 BSSE correction

In the FMO method, an correction of the basis set super-position error (BSSE) is not simple because the monomer and dimer calculations include the environmental electrostatic potential. Additionally, in the case including the cut of covalent bonds, the BSSE correction becomes still more difficult because several basis sets are shared by the two fragments. Thus, in the **PAICS**, amount of the BSSE is estimated under the vacuum condition for the IFIE of the pairs not sharing the basis sets. For the estimation of the BSSE of the fragment pair IJ , the following values are additionally needed:

$E_{I(IJ)}^{HF(vac)}$: the monomer energy of the I -th fragment under the vacuum condition including the basis set of the J -th fragment.

$E_{J(IJ)}^{HF(vac)}$: the monomer energy of the J -th fragment under the vacuum condition including the basis set of the I -th fragment.

$E_I^{HF(vac)}$: the monomer energy of the I -th fragment under the vacuum condition.

$E_J^{HF(vac)}$: the monomer energy of the J -th fragment under the vacuum condition.

Using these values, the BSSE of the IFIE between the fragments I and J is written as the following equation:

$$E_{IJ}^{BSSE(HF)} = E_{I(IJ)}^{HF(vac)} - E_I^{HF(vac)} + E_{J(IJ)}^{HF(vac)} - E_J^{HF(vac)} \quad (4.1.69)$$

Thus, the corrected IFIE is

$$\Delta E_{IJ}^{HF(CP)} = \Delta E_{IJ}^{HF} - E_{IJ}^{BSSE(HF)} \quad (4.1.70)$$

4.2 FMO–RHF (gradient)

In this section, the theory related to the calculation of the FMO–RHF gradient is explained, making it be related to the output of the **PAICS**. The formulation basically follows the previous publications reporting the theory and method of the FMO scheme [1, 8, 9, 10, 11, 12, 13].

4.2.1 Definition of the U_{mi}^A

We write the derivative of the orbital coefficients as

$$\frac{\partial}{\partial A} C_{X\mu i}^{HF} = \sum_{m \in X}^{all} U_{mi}^A C_{X\mu m}^{HF}, \quad (4.2.1)$$

where, the following equation is satisfied:

$$U_{ij}^A + U_{ji}^A = - \sum_{\mu\nu \in X} C_{X\mu i}^{HF} C_{X\nu j}^{HF} \left(\frac{\partial}{\partial A} S_{X\mu\nu} \right). \quad (4.2.2)$$

4.2.2 Derivative of the FMO energy

From Eq. (4.1.26), the following equation is obtained:

$$E_{fmo2}^{HF} = -(N_f - 2) \sum_I E_I'^{HF} + \sum_{I>J} \left\{ E_{IJ}'^{HF} + Tr(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{V}_{IJ}) \right\}. \quad (4.2.3)$$

Here, we introduce a new matrix defined as

$$\mathbf{D}_{(IJ)}^{HF} = \mathbf{D}_{I(J)}^{HF} + \mathbf{D}_{J(I)}^{HF}, \quad (4.2.4)$$

and using this matrix, Eq. (4.2.3) is written as

$$E_{fmo2}^{HF} = -(N_f - 2) \sum_I E_I'^{HF} + \sum_{I>J} \left\{ E_{IJ}^{HF} - Tr(\mathbf{D}_{(IJ)}^{HF} \mathbf{V}_{IJ}^{HF}) \right\}. \quad (4.2.5)$$

Thus, the FMO2-RHF gradient could be obtained as a derivative of this equation:

$$\frac{\partial}{\partial A} E_{fmo2}^{HF} = -(N_f - 2) \sum_I \frac{\partial}{\partial A} E_I'^{HF} + \sum_{I>J} \frac{\partial}{\partial A} \left\{ E_{IJ}^{HF} - Tr(\mathbf{D}_{(IJ)}^{HF} \mathbf{V}_{IJ}^{HF}) \right\}. \quad (4.2.6)$$

< Derivative of $E_I'^{HF}$ >

The derivative of the $E_I'^{HF}$ is written as

$$\frac{\partial}{\partial A} E_I'^{HF} = \frac{\partial}{\partial A} E_I^{HF} - \sum_{\mu\nu} \left(\frac{\partial}{\partial A} D_{\mu\nu}^I \right) V_{\mu\nu}^I - \sum_{\mu\nu} D_{\mu\nu}^I \left(\frac{\partial}{\partial A} V_{\mu\nu}^I \right). \quad (4.2.7)$$

Because derivative of E_I^{HF} is calculated as a normal RHF energy gradient, we obtain the following equation:

$$\begin{aligned} \frac{\partial}{\partial A} E_I'^{HF} = & \sum_{\mu\nu \in I} D_{\mu\nu}^{HF} \left(\frac{\partial}{\partial A} h_{I\mu\nu} \right) \\ & + \frac{1}{2} \sum_{\mu\nu\lambda\sigma \in I} (D_{\mu\nu}^{HF} D_{\lambda\sigma}^{HF} - \frac{1}{2} D_{\nu\lambda}^{HF} D_{\mu\sigma}^{HF}) \frac{\partial}{\partial A} (\mu\nu | \lambda\sigma) \\ & - 2 \sum_{\mu\nu \in I} W_{\mu\nu}^{HF} \frac{\partial}{\partial A} S_{I\mu\nu} - \sum_{\mu\nu \in I} \left(\frac{\partial}{\partial A} D_{\mu\nu}^{HF} \right) V_{I\mu\nu}, \end{aligned} \quad (4.2.8)$$

where the derivative of the projection operator is neglected and $\mathbf{W}_X^{HF}$ is

$$\mathbf{W}_X^{HF} = \frac{1}{4} \mathbf{D}_X^{HF} \mathbf{F}_X \mathbf{D}_X^{HF}. \quad (4.2.9)$$

As we shall see below, the last term is canceled with the terms from the dimer parts of Eq. (4.2.17). It should be noted that the derivative of the environmental electrostatic potential ($\mathbf{V}_X$) is not needed for the derivative of $E_I'^{HF}$.

< Derivative of E_{IJ}^{HF} >

Because the derivative of the E_{IJ}^{HF} is calculated as a normal RHF gradient, its derivative is written as the following equation:

$$\begin{aligned} \frac{\partial}{\partial A} E_{IJ}^{HF} = & \sum_{\mu\nu \in IJ} D_{\mu\nu}^{HF} \left(\frac{\partial}{\partial A} h_{IJ\mu\nu} \right) \\ & + \frac{1}{2} \sum_{\mu\nu\lambda\sigma \in IJ} (D_{\mu\nu}^{HF} D_{\lambda\sigma}^{HF} - \frac{1}{2} D_{\nu\lambda}^{HF} D_{\mu\sigma}^{HF}) \frac{\partial}{\partial A} (\mu\nu | \lambda\sigma) \\ & - 2 \sum_{\mu\nu \in IJ} W_{\mu\nu}^{HF} \frac{\partial}{\partial A} S_{IJ\mu\nu} + \sum_{\mu\nu \in IJ} D_{\mu\nu}^{HF} \left(\frac{\partial}{\partial A} V_{IJ\mu\nu} \right), \end{aligned} \quad (4.2.10)$$

where the derivative of the projection operator is neglected. In the case of E_{IJ}^{HF} , the derivative of the environmental electrostatic potential is needed (the last term of this equation).

< **Derivative of $Tr(\mathbf{D}_{(IJ)}^{HF} \mathbf{V}_{IJ})$** >

We note the following relation:

$$\begin{aligned}
\sum_{I < J} \mathbf{D}_{(IJ)} \mathbf{V}_{IJ} &= \sum_{I < J} \left(\mathbf{D}_{I(J)}^{HF} \mathbf{V}_{IJ} + \mathbf{D}_{J(I)}^{HF} \mathbf{V}_{IJ} \right) \\
&= \sum_{I < J} \left(\mathbf{D}_I^{HF} \mathbf{V}_I + \mathbf{D}_J^{HF} \mathbf{V}_J \right) - \sum_{I < J} \left(\mathbf{D}_I^{HF} \mathbf{V}_{I(J)} + \mathbf{D}_J^{HF} \mathbf{V}_{J(I)} \right) \\
&= (N_f - 1) \sum_I \mathbf{D}_I^{HF} \mathbf{V}_I - \sum_I \sum_{I \neq J} \mathbf{D}_I^{HF} \mathbf{V}_{I(J)} \\
&= (N_f - 1) \sum_I \mathbf{D}_I^{HF} \mathbf{V}_I - \sum_I \mathbf{D}_I^{HF} \mathbf{V}_I \\
&= (N_f - 2) \sum_I \mathbf{D}_I^{HF} \mathbf{V}_I.
\end{aligned} \tag{4.2.11}$$

Using this relation, the derivative of the term including $Tr(\mathbf{D}_{(IJ)}^{HF} \mathbf{V}_{IJ})$ in Eq. (4.2.17) is

$$\begin{aligned}
- \sum_{I > J} \frac{\partial}{\partial A} Tr(\mathbf{D}_{(IJ)}^{HF} \mathbf{V}_{IJ}) &= \\
&= - \sum_{I > J} \sum_{\mu\nu \in IJ} D_{(IJ)}^{HF}{}_{\mu\nu} \left(\frac{\partial}{\partial A} V_{IJ\mu\nu} \right) - (N_f - 2) \sum_{\mu\nu \in I} \left(\frac{\partial}{\partial A} D_I^{HF}{}_{\mu\nu} \right) V_{I\mu\nu}.
\end{aligned} \tag{4.2.12}$$

< **Terms including the derivative of density matrix** >

Terms including the derivative of density matrix are the last terms of Eq. (4.2.8) and the last term of Eq. (4.2.12), i.e.,

$$(N - 2_f) \sum_{\mu\nu \in I} \left(\frac{\partial}{\partial A} D_I^{HF}{}_{\mu\nu} \right) V_{I\mu\nu} - (N - 2_f) \sum_{\mu\nu \in I} \left(\frac{\partial}{\partial A} D_I^{HF}{}_{\mu\nu} \right) V_{I\mu\nu} = 0. \tag{4.2.13}$$

Thus, they are canceled.

< **Terms including the environmental electrostatic potential** >

Terms including the derivative of environmental electrostatic potential is the last term of Eq. (4.2.10) and the first term of Eq. (4.2.12), i.e.,

$$\sum_{\mu\nu \in IJ} D_{IJ}^{HF}{}_{\mu\nu} \left(\frac{\partial}{\partial A} V_{IJ\mu\nu} \right) - \sum_{\mu\nu \in IJ} D_{(IJ)}^{HF}{}_{\mu\nu} \left(\frac{\partial}{\partial A} V_{IJ\mu\nu} \right) = \sum_{\mu\nu \in IJ} \Delta D_{IJ}^{HF}{}_{\mu\nu} \left(\frac{\partial}{\partial A} V_{IJ\mu\nu} \right). \tag{4.2.14}$$

< **definition $G_X^{HF}(A)$** >

Here, we introduce the following values:

$$\begin{aligned}
G_I^{HF}(A) &= \sum_{\mu\nu \in I} D_I^{HF}{}_{\mu\nu} \left(\frac{\partial}{\partial A} h_{I\mu\nu} \right) \\
&+ \frac{1}{2} \sum_{\mu\nu\lambda\sigma \in I} \left(D_I^{HF}{}_{\mu\nu} D_I^{HF}{}_{\lambda\sigma} - \frac{1}{2} D_I^{HF}{}_{\nu\lambda} D_I^{HF}{}_{\nu\sigma} \right) \frac{\partial}{\partial A} (\mu\nu | \lambda\sigma) \\
&- 2 \sum_{\mu\nu \in I} W_I^{HF}{}_{\mu\nu} \left(\frac{\partial}{\partial A} S_{I\mu\nu} \right)
\end{aligned} \tag{4.2.15}$$

$$\begin{aligned}
G_{IJ}^{HF}(A) = & \sum_{\mu\nu \in IJ} D_{IJ\mu\nu}^{HF} \left(\frac{\partial}{\partial A} h_{IJ\mu\nu} \right) \\
& + \frac{1}{2} \sum_{\mu\nu\lambda\sigma \in IJ} \left(D_{IJ\mu\nu}^{HF} D_{IJ\lambda\sigma}^{HF} - \frac{1}{2} D_{IJ\nu\lambda}^{HF} D_{IJ\nu\sigma}^{HF} \right) \frac{\partial}{\partial A} (\mu\nu | \lambda\sigma) \\
& - 2 \sum_{\mu\nu \in IJ} W_{IJ\mu\nu}^{HF} \left(\frac{\partial}{\partial A} S_{IJ\mu\nu} \right) + \sum_{\mu\nu \in IJ} \Delta D_{IJ\mu\nu}^{HF} \left(\frac{\partial}{\partial A} V_{IJ\mu\nu} \right) \quad (4.2.16)
\end{aligned}$$

Using these values, the FMO2-RHF gradient is written as

$$\frac{\partial}{\partial A} E_{fmo2}^{HF} = -(N_f - 2) \sum_I G_I^{HF}(A) + \sum_{I>J} G_{IJ}^{HF}(A). \quad (4.2.17)$$

4.2.3 Dimer-es approxmition

In the case of the dimer-es pairs, E_{IJ}^{HF} is written as

$$E_{IJ}^{HF} = E'_{IJ}{}^{HF} + Tr \left(\mathbf{D}_{(IJ)}^{HF} \mathbf{V}_{IJ} \right). \quad (4.2.18)$$

Thus, we need to calculate the following value:

$$\frac{\partial}{\partial A} E'_{IJ}{}^{HF}. \quad (4.2.19)$$

$E'_{IJ}{}^{HF}$ is given as Eq. (4.1.30). Because parts including the derivative of density matrix is canceled, we need to calculate the remaining parts. Thus, in the case of the dimer-es pairs,

$$\begin{aligned}
G_{IJ}^{HF}(A) = & G_I^{HF}(A) + G_J^{HF}(A) \\
& + \sum_{\mu\nu \in J} D_{I\mu\nu}^{HF} \left(\frac{\partial}{\partial A} u_{J\mu\nu} \right) + \sum_{\mu\nu \in J} D_{J\mu\nu}^{HF} \left(\frac{\partial}{\partial A} u_{I\mu\nu} \right) \\
& + \sum_{\mu\nu \in I} \sum_{\lambda\sigma \in J} D_{I\mu\nu}^{HF} D_{J\lambda\sigma}^{HF} \frac{\partial}{\partial A} (\mu\nu | \lambda\sigma) \quad (4.2.20)
\end{aligned}$$

4.2.4 Environmental electrostatic potential

Because the environmental electrostatic potential is evaluated with the three types of manner as shown in Eq. (4.1.34) and (4.1.36), this is written as the following equation:

$$\begin{aligned}
\sum_{\mu\nu \in X} \Delta D_{X\mu\nu}^{HF} \frac{\partial}{\partial A} V_{X\mu\nu} = & \sum_{\mu\nu \in X} \Delta D_{X\mu\nu}^{HF} \frac{\partial}{\partial A} \sum_{K \neq X} u_{X(K)\mu\nu} + \sum_{\mu\nu \in X} \Delta D_{X\mu\nu}^{HF} \frac{\partial}{\partial A} \sum_{K_4} v_{X(K_4)\mu\nu}^4 \\
& + \sum_{\mu\nu \in X} \Delta D_{X\mu\nu}^{HF} \frac{\partial}{\partial A} \sum_{K_3} v_{X(K_3)\mu\nu}^3 + \sum_{\mu\nu \in X} \Delta D_{X\mu\nu}^{HF} \frac{\partial}{\partial A} \sum_{K_p} v_{X(K_p)\mu\nu}^p. \quad (4.2.21)
\end{aligned}$$

< **derivative of $\mathbf{u}_{X(K)}$** >

The derivative of $\mathbf{u}_{X(K)}$ is

$$\frac{\partial}{\partial A} \sum_{K \neq X} \mathbf{u}_{X(K)\mu\nu} = \frac{\partial}{\partial A} \langle \mu | \sum_{K \neq X} \sum_{B \in K} \frac{-Z_B}{|\mathbf{R}_B - \mathbf{r}_1|} | \nu \rangle. \quad (4.2.22)$$

Thus, the first term of Eq. (4.2.21) is expressed as

$$\begin{aligned} \sum_{\mu\nu \in X} \Delta D_{X\mu\nu}^{HF} \frac{\partial}{\partial A} \sum_{K \neq X} u_{X(K)\mu\nu} = \\ \sum_{\mu\nu \in X} \Delta D_{X\mu\nu}^{HF} \sum_{K \neq X} \sum_{B \in K} \left\{ \left\langle \left(\frac{\partial}{\partial A} \mu \right) \middle| \frac{-Z_B}{|\mathbf{R}_B - \mathbf{r}_1|} \middle| \nu \right\rangle \right. \\ \left. + \left\langle \mu \middle| \frac{-Z_B}{|\mathbf{R}_B - \mathbf{r}_1|} \middle| \left(\frac{\partial}{\partial A} \nu \right) \right\rangle + \left\langle \mu \middle| \left(\frac{\partial}{\partial A} \frac{-Z_B}{|\mathbf{R}_B - \mathbf{r}_1|} \right) \middle| \nu \right\rangle \right\}. \end{aligned} \quad (4.2.23)$$

< **derivative of** $\mathbf{v}_{X(K_4)}^4$ >

The derivative of $v_{X(K_4)\mu\nu}^4$ is

$$\begin{aligned} \frac{\partial}{\partial A} \sum_{K_4} v_{X(K_4)\mu\nu}^4 = \sum_{K_4} \sum_{\lambda\sigma \in K_4} \left\{ \left(\frac{\partial}{\partial A} D_{K_4\lambda\sigma}^{HF} \right) (\mu\nu | \lambda\sigma) + \right. \\ \left. D_{K_4\lambda\sigma}^{HF} \frac{\partial}{\partial A} (\mu\nu | \lambda\sigma) \right\}. \end{aligned} \quad (4.2.24)$$

The first term of this equation is written using the U_{ij}^A as

$$4 \sum_{K_4} \sum_{i \in K_4} \sum_{m \in K_4}^{occ} U_{mi}^A (\mu\nu | im) + 4 \sum_{K_4} \sum_{i \in K_4} \sum_{m \in K_4}^{vir} U_{mi}^A (\mu\nu | im). \quad (4.2.25)$$

If we neglect the second term, this is written as

$$-2 \sum_{K_4} \sum_{i \in K_4} \sum_{m \in K_4}^{occ} \left\{ \sum_{\alpha\beta \in K_4} C_{X\alpha m}^{HF} C_{X\beta i}^{HF} \left(\frac{\partial}{\partial A} S_{X\alpha\beta} \right) \right\} (\mu\nu | im). \quad (4.2.26)$$

When using the density matrix, this is written as

$$-2 \sum_{K_4} \sum_{\lambda\sigma \in K_4} \left\{ \frac{1}{4} \sum_{\alpha\beta \in K_4} D_{K_4\lambda\alpha}^{HF} \left(\frac{\partial}{\partial A} S_{X\alpha\beta} \right) D_{K_4\beta\sigma}^{HF} \right\} (\mu\nu | \lambda\sigma). \quad (4.2.27)$$

Consequently, the second term of Eq. (4.2.21) can be expressed as the following equation:

$$\begin{aligned} \sum_{\mu\nu \in X} \Delta D_{X\mu\nu}^{HF} \frac{\partial}{\partial A} \sum_{K_4} v_{X(K_4)\mu\nu}^4 = \\ \sum_{\mu\nu \in X} \sum_{K_4} \sum_{\lambda\sigma \in K_4} \Delta D_{X\mu\nu}^{HF} D_{K_4\lambda\sigma}^{HF} \frac{\partial}{\partial A} (\mu\nu | \lambda\sigma) \\ - 2 \sum_{K_4} \sum_{\alpha\beta \in K_4} \left\{ \sum_{\lambda\sigma \in K_4} \frac{1}{4} D_{K_4\alpha\lambda}^{HF} T_{X(K_4)\lambda\sigma}^4 D_{K_4\sigma\beta}^{HF} \right\} \frac{\partial}{\partial A} S_{X\alpha\beta}, \end{aligned} \quad (4.2.28)$$

where

$$T_{X(K_4)\lambda\sigma}^4 = \sum_{\mu\nu \in X} \Delta D_{X\mu\nu}^{HF} (\mu\nu | \lambda\sigma). \quad (4.2.29)$$

< **derivative of** $\mathbf{v}_{X(K_4)}^3$ >

The derivative of $v_{X(K_3)\mu\nu}^3$ is

$$\begin{aligned} \sum_{K_3} \frac{\partial}{\partial A} v_{X(K_3)\mu\nu}^3 = \sum_{K_3} \sum_{\lambda\sigma \in K_3} \left\{ \left(\frac{\partial}{\partial A} D_{K_3\lambda\sigma}^{HF} \right) S_{X\sigma\lambda}(\mu\nu|\lambda\lambda) + \right. \\ \left. D_{K_3\lambda\sigma}^{HF} \left(\frac{\partial}{\partial A} S_{X\sigma\lambda} \right) (\mu\nu|\lambda\lambda) + D_{K_3\lambda\sigma}^{HF} S_{X\sigma\lambda} \frac{\partial}{\partial A} (\mu\nu|\lambda\lambda) \right\}. \end{aligned} \quad (4.2.30)$$

The first term of this equation is written using the U_{ij}^A as

$$\begin{aligned} 4 \sum_{K_3} \sum_{\lambda\sigma \in K_3} \sum_{i \in K_3}^{occ} \sum_{m \in K_3}^{occ} U_{mi}^A C_{X\lambda m}^{HF} C_{X\sigma i}^{HF} S_{X\lambda\sigma}(\mu\nu|\lambda\lambda) \\ + 4 \sum_{K_3} \sum_{\lambda\sigma \in K_3} \sum_{i \in K_3}^{occ} \sum_{m \in K_3}^{vir} U_{mi}^A C_{X\lambda m}^{HF} C_{X\sigma i}^{HF} S_{X\lambda\sigma}(\mu\nu|\lambda\lambda). \end{aligned} \quad (4.2.31)$$

If we neglect the second term, this is written as

$$\begin{aligned} -2 \sum_{K_3} \sum_{\lambda\sigma \in K_3} \sum_{i \in K_3}^{occ} \sum_{m \in K_3}^{occ} \left(\sum_{\alpha\beta \in K_3} C_{X\alpha i}^{HF} C_{X\beta m}^{HF} \frac{\partial}{\partial A} S_{X\alpha\beta} \right) \times \\ C_{X\lambda m}^{HF} C_{X\sigma i}^{HF} S_{X\sigma\lambda}(\mu\nu|\lambda\lambda) \end{aligned} \quad (4.2.32)$$

When using the density matrix, this is written as

$$-2 \sum_{K_3} \sum_{\lambda \in K_3} \sum_{\sigma \in K_3} \sum_{\alpha\beta \in K_3} D_{K_3\lambda\alpha}^{HF} \left(\frac{\partial}{\partial A} S_{X\alpha\beta} \right) D_{K_3\beta\sigma}^{HF} S_{X\sigma\lambda}(\mu\nu|\lambda\lambda) \quad (4.2.33)$$

Consequently, the third term of Eq. (4.2.21) can be expressed as the following equation:

$$\begin{aligned} \sum_{\mu\nu \in X} \Delta D_{X\mu\nu}^{HF} \frac{\partial}{\partial A} \sum_{K_3} v_{X(K_3)\mu\nu}^3 = \\ \sum_{\mu\nu \in X} \sum_{K_3} \sum_{\lambda \in K_3} \Delta D_{X\mu\nu}^{HF} \left(\sum_{\sigma \in K_3} D_{K_3\lambda\sigma}^{HF} S_{X\sigma\lambda} \right) \frac{\partial}{\partial A} (\mu\nu|\lambda\lambda) \\ - 2 \sum_{K_3} \sum_{\alpha\beta \in K_3} \left\{ \frac{1}{4} \sum_{\lambda\sigma \in K_3} D_{K_3\alpha\lambda}^{HF} T_{X(K_3)\lambda\lambda}^3 S_{X\lambda\sigma} D_{K_3\sigma\beta}^{HF} \right. \\ \left. - \frac{1}{2} T_{X(K_3)\alpha\alpha}^3 D_{K_3\alpha\beta}^{HF} \right\} \frac{\partial}{\partial A} S_{X\alpha\beta}, \end{aligned} \quad (4.2.34)$$

where

$$T_{X(K_3)\lambda\lambda}^3 = \sum_{\mu\nu \in X} \Delta D_{X\mu\nu}^{HF} (\mu\nu|\lambda\lambda). \quad (4.2.35)$$

$\langle \text{derivative of } \mathbf{v}_{X(K_p)}^p \rangle$

The derivative of $v_{X(K_p)\mu\nu}^p$ is

$$\frac{\partial}{\partial A} \sum_{K_p} v_{X(K_p)\mu\nu}^p = \sum_{K_p} \sum_{B \in K_p} \left\{ \left(\frac{\partial}{\partial A} p_B \right) \langle \mu | \frac{1}{|\mathbf{R}_B - \mathbf{r}_1|} | \nu \rangle + p_B \frac{\partial}{\partial A} \langle \mu | \frac{1}{|\mathbf{R}_B - \mathbf{r}_1|} | \nu \rangle \right\} \quad (4.2.36)$$

If we neglect the first term of this equation, the fourth term of Eq. (4.2.21) can be expressed as the following equation:

$$\begin{aligned} \sum_{\mu\nu \in X} \Delta D_{X\mu\nu}^{HF} \frac{\partial}{\partial A} \sum_{K_p} v_{X(K_p)\mu\nu}^p = \\ \sum_{\mu\nu \in X} \Delta D_{X\mu\nu}^{HF} \sum_{K_p} \sum_{B \in K_p} \left\{ \left(\frac{\partial}{\partial A} \mu \right) \langle \mu | \frac{p_B}{|\mathbf{R}_B - \mathbf{r}_1|} | \nu \rangle + \right. \\ \left. \langle \mu | \frac{p_B}{|\mathbf{R}_B - \mathbf{r}_1|} \left(\frac{\partial}{\partial A} \nu \right) \rangle + \langle \mu | \left(\frac{\partial}{\partial A} \frac{p_B}{|\mathbf{R}_B - \mathbf{r}_1|} \right) | \nu \rangle \right\}. \end{aligned} \quad (4.2.37)$$

4.2.5 External electrostatic potential

In the case that external electrostatic potential exists, $\mathbf{h}^X$ is modified as

$$\mathbf{h}_X \rightarrow \mathbf{h}_X + \mathbf{V}_X^{ext}. \quad (4.2.38)$$

Thus, the following electrostatic term is added to $G_X^{HF}(A)$:

$$\sum_{\mu\nu \in X} D_{X\mu\nu}^{HF} \frac{\partial}{\partial A} V_{X\mu\nu}^{ext}, \quad (4.2.39)$$

Consequently, the following value is added to the FMO2-RHF gradient:

$$-(N_f - 2) \sum_I \sum_{\mu\nu \in I} D_{I\mu\nu}^{HF} \frac{\partial}{\partial A} V_{I\mu\nu}^{ext} + \sum_{I < J} \sum_{\mu\nu \in IJ} D_{IJ\mu\nu}^{HF} \frac{\partial}{\partial A} V_{IJ\mu\nu}^{ext} \quad (4.2.40)$$

4.2.6 Nucleus potential

The expression of the FMO2-RHF gradient including the external electrostatic potential and nucleus potential is the following equation:

$$\begin{aligned} \frac{\partial}{\partial A} E_{fmo2}^{HF(ext+Z)} = \frac{\partial}{\partial A} E_{fmo2}^{HF} \\ -(N_f - 2) \sum_I \sum_{\mu\nu \in I} D_{I\mu\nu}^{HF} \frac{\partial}{\partial A} V_{I\mu\nu}^{ext} + \sum_{I < J} \sum_{\mu\nu \in IJ} D_{IJ\mu\nu}^{HF} \frac{\partial}{\partial A} V_{IJ\mu\nu}^{ext} \\ + \frac{\partial}{\partial A} \left(\sum_I E_I^{ZZ} + \sum_{I < J} E_{IJ}^{ZZ} + \sum_I E_I^{Zext} \right). \end{aligned} \quad (4.2.41)$$

4.2.7 Restriction of dimer calculation

When dividing the fragments into two groups (F_1 and F_2), we defined the partial energy of F_1 as Eq. (4.1.68). Thus, the "partial energy gradient" of the atoms in F_1 can be defined as the following equation:

$$\begin{aligned} \frac{\partial}{\partial A} E_{fmo2(F_1)}^{HF} = & -(N_{f_1} - 2) \sum_I G_I^{HF}(A) + \sum_{I>J} G_{IJ}^{HF}(A) + \\ & \sum_I \sum_K G_{IK}^{HF}(A) - N_{f_2} \sum_I G_I^{HF}(A) - N_{f_1} \sum_K G_K^{HF}(A), \end{aligned} \quad (4.2.42)$$

where IJ and KL are the indexes of the fragments in F_1 and F_2 , respectively, and A is the geometrical parameters of the atoms of the fragments in F_1 . Difference between the normal energy gradient (Eq. (4.2.17)) and partial energy gradient is

$$-(N_{f_1} - 2) \sum_K G_K^{HF}(A) + \sum_{K>L} G_{KL}^{HF}(A). \quad (4.2.43)$$

As show in the previous section, the terms including derivative of the density matrix dose not need to be calculated in the case of the normal energy gradient, i.e., the last term of Eq. (4.2.8) and the second term of Eq. (4.2.12) are canceled with each other. But in the case of the partial energy gradient, the following terms are remained because of the above difference:

$$\sum_K \sum_I \sum_{\mu\nu \in K} \left(\frac{\partial}{\partial A} D_{K\mu\nu}^{HF} \right) V_{K(I)\mu\nu} \quad (4.2.44)$$

If we want to calculate the partial energy gradient exactly, this term must be evaluated. But, this term is treated as zero in the **PAICS**. It is consider that when using the partial energy gradient for geometry optimizations or molecular dynamics simulations, we need the "gradient close to the total gradient" rather than the "exact partial gradient".

4.3 FMO–RHF (density)

In this section, the theory related to the calculation of the electron density, electrostatic potential, and electric field of the FMO–RHF is explained, making it be related to the output of the **PAICS**. The formulation basically follows the previous publications reporting the theory and method of the FMO scheme [1].

4.3.1 Electron density

The electron density of the monomer or dimer is written as

$$\rho_X^{HF}(\mathbf{r}_m) = \sum_{i \in X}^{occ.} n_i | \tilde{\psi}_X^{HF}(\mathbf{r}_m) \tilde{\psi}_X^{HF}(\mathbf{r}_m) |, \quad (4.3.1)$$

where $\tilde{\psi}_X^i(\mathbf{r})$ is the molecular orbital of monomer or dimer, and n_i is occupation number (i.e., 2 in the case of RHF calculation). Using the density matrix, this equation is written as

$$\rho_X^{HF}(\mathbf{r}_m) = \sum_{\mu\nu \in X} \mathbf{D}_X^{HF}{}_{\mu\nu} \mu(\mathbf{r}_m) \nu(\mathbf{r}_m). \quad (4.3.2)$$

FMO1 density is defined as

$$\rho_{fmo1}^{HF}(\mathbf{r}_m) = \sum_I \rho_I^{HF}(\mathbf{r}_m). \quad (4.3.3)$$

FMO2 density is defined as

$$\rho_{fmo2}^{HF}(\mathbf{r}_m) = \sum_{I>J} \rho_{IJ}^{HF}(\mathbf{r}_m) - (N-2) \sum_I \rho_I^{HF}(\mathbf{r}_m). \quad (4.3.4)$$

The FMO2 density is rewritten as

$$\rho_{fmo2}^{HF}(\mathbf{r}_m) = \rho_{fmo1}^{HF}(\mathbf{r}_m) + \sum_{I>J} \left\{ \rho_{IJ}^{HF}(\mathbf{r}_m) - \rho_I^{HF}(\mathbf{r}_m) - \rho_J^{HF}(\mathbf{r}_m) \right\}. \quad (4.3.5)$$

Here, we introduce $\Delta\rho^{IJ}(\mathbf{r})$ defined as

$$\Delta\rho_{IJ}^{HF}(\mathbf{r}_m) = \rho_{IJ}^{HF}(\mathbf{r}_m) - \rho_I^{HF}(\mathbf{r}_m) - \rho_J^{HF}(\mathbf{r}_m) = \sum_{\mu\nu \in IJ} \Delta\mathbf{D}_{IJ}^{HF}{}_{\mu\nu} \mu(\mathbf{r}_m) \nu(\mathbf{r}_m). \quad (4.3.6)$$

Consequently, the FMO2 density is written as:

$$\rho_{fmo2}^{HF}(\mathbf{r}_m) = \rho_{fmo1}^{HF}(\mathbf{r}_m) + \sum_{I>J} \Delta\rho_{IJ}^{HF}(\mathbf{r}_m). \quad (4.3.7)$$

We should note that the second term of the FMO2-RHF electron density in Eq. (4.3.7) is two-body correction on the FMO1-RHF electron density.

4.3.2 Electrostatic potential

The electrostatic potential at position $\mathbf{r}_m$ is written as the following equation:

$$\phi^{HF}(\mathbf{r}_m) = \int \frac{-\rho^{HF}(\mathbf{r})}{|\mathbf{r}_m - \mathbf{r}|} d\mathbf{r}. \quad (4.3.8)$$

Since the electron density of the FMO method are (4.3.3) and (4.3.7), we obtain the following expressions for the electrostatic potentials of the FMO1 and FMO2:

$$\phi_{fmo1}^{HF}(\mathbf{r}_m) = \sum_I \sum_{\mu\nu \in I} D_{I\mu\nu}^{HF} \langle \mu | \frac{-1}{|\mathbf{r}_m - \mathbf{r}|} | \nu \rangle, \quad (4.3.9)$$

$$\phi_{fmo2}^{HF}(\mathbf{r}_m) = \phi_{fmo1}^{HF}(\mathbf{r}_m) + \sum_{I>J} \sum_{\mu\nu \in IJ} \Delta D_{IJ\mu\nu}^{HF} \langle \mu | \frac{-1}{|\mathbf{r}_m - \mathbf{r}|} | \nu \rangle. \quad (4.3.10)$$

Here, we introduce a new matrix $\mathbf{u}_X(\mathbf{r}_m)$ defined as

$$u_{X\mu\nu}(\mathbf{r}_m) = \langle \mu | \frac{-1}{|\mathbf{r}_m - \mathbf{r}|} | \nu \rangle. \quad (4.3.11)$$

Using this value, the following expressions is obtained:

$$\phi_{fmo1}^{HF}(\mathbf{r}_m) = \sum_I \text{Tr}(\mathbf{D}_I^{HF} \mathbf{u}_I(\mathbf{r}_m)), \quad (4.3.12)$$

$$\phi_{fmo2}^{HF}(\mathbf{r}_m) = \phi_{fmo1}^{HF}(\mathbf{r}_m) + \sum_{I>J} \text{Tr}(\Delta\mathbf{D}_{IJ}^{HF} \mathbf{u}_{IJ}(\mathbf{r}_m)). \quad (4.3.13)$$

Note that the second term of the FMO2-RHF electrostatic potential is two-body correction on the FMO1-RHF electrostatic potential.

4.3.3 Electric field

The electric field at position $\mathbf{r}$ is written as the following equation:

$$\mathbf{E}(\mathbf{r}) = -\frac{\partial}{\partial \mathbf{r}}\phi(\mathbf{r}) \quad (4.3.14)$$

Since the electrostatic potential obtained from the FMO method are (4.3.12) and (4.5.16), we obtain the following expressions for the electric field of the FMO1 and FMO2:

$$\mathbf{E}_{fmo1}^{HF}(\mathbf{r}_m) = -\sum_I Tr\left\{\mathbf{D}_I^{HF}\left(\frac{\partial}{\partial \mathbf{r}_m}\mathbf{u}_I(\mathbf{r}_m)\right)\right\}, \quad (4.3.15)$$

$$\mathbf{E}_{fmo2}^{HF}(\mathbf{r}_m) = \mathbf{E}_{fmo1}^{HF}(\mathbf{r}_m) - \sum_{I>J} Tr\left\{\Delta\mathbf{D}_{IJ}^{HF}\left(\frac{\partial}{\partial \mathbf{r}_m}\mathbf{u}_{IJ}(\mathbf{r}_m)\right)\right\}. \quad (4.3.16)$$

Note that the second term of the FMO2-RHF electric field is two-body correction on the FMO1-RHF electric field.

4.3.4 Mulliken population analysis

The total electron number is written as the following equation:

$$N^{HF} = \int \rho^{HF}(\mathbf{r}) d\mathbf{r}. \quad (4.3.17)$$

Since the electron density of the FMO method are (4.3.3) and (4.3.7), the total electron number is written as

$$N_{fmo1}^{HF} = \sum_I \sum_{\mu \in I} \left(\mathbf{D}_I^{HF} \mathbf{S}_I\right)_{\mu\mu}, \quad (4.3.18)$$

$$N_{fmo2}^{HF} = N_{fmo1}^{HF} + \sum_{I>J} \sum_{\mu \in IJ} \left(\Delta\mathbf{D}_{IJ}^{HF} \mathbf{S}_{IJ}\right)_{\mu\mu}, \quad (4.3.19)$$

where

$$N^{HF} = N_{fmo1}^{HF} = N_{fmo2}^{HF}. \quad (4.3.20)$$

Thus, we obtain the following expression for the electron population of atom A of the FMO1 and FMO2:

$$N_{fmo1}^{HF}(A) = \sum_I \sum_{\mu \in A} \left(\mathbf{D}_I^{HF} \mathbf{S}_I\right)_{\mu\mu}, \quad (4.3.21)$$

$$N_{fmo2}^{HF}(A) = N_{fmo1}^{HF}(A) + \sum_{I>J} \sum_{\mu \in A} \left(\Delta\mathbf{D}_{IJ}^{HF} \mathbf{S}_{IJ}\right)_{\mu\mu}, \quad (4.3.22)$$

Here, we introduce N_I^{HF} and ΔN_{IJ}^{HF} defined as the following equations:

$$N_I^{HF}(A) = \sum_{\mu \in A} \left(\mathbf{D}_I^{HF} \mathbf{S}_I\right)_{\mu\mu}, \quad (4.3.23)$$

$$\Delta N_{IJ}^{HF}(A) = \sum_{\mu \in A} \left(\Delta \mathbf{D}_{IJ}^{HF} \mathbf{S}_{IJ} \right)_{\mu\mu} \quad (4.3.24)$$

Using these values, the following expression is obtained:

$$N_{fmo1}^{HF}(A) = \sum_I N_I^{HF}, \quad (4.3.25)$$

$$N_{fmo2}^{HF}(A) = N_{fmo1}^{HF}(A) + \sum_{I>J} \Delta N_{IJ}^{HF}(A). \quad (4.3.26)$$

We should note that the second term of the FMO2 population is two-body correction on the FMO1 population.

4.4 FMO–MP2

In this section, the theory related to the FMO–MP2 is explained, making it be related to the output of the **PAICS**. The formulation basically follows the previous publications reporting the theory and method of the FMO scheme [14, 15, 16, 7].

4.4.1 Energy

The MP2 total energy of one-body approximation (FMO1–MP2) and two-body approximation (FMO–MP2) is

$$E_{fmo1}^{MP2} = E_{fmo1}^{HF} + E_{fmo1}^{corr(MP2)}, \quad (4.4.1)$$

$$E_{fmo2}^{MP2} = E_{fmo2}^{HF} + E_{fmo2}^{corr(MP2)}. \quad (4.4.2)$$

Here, $E_{fmo1}^{corr(MP2)}$ and $E_{fmo2}^{corr(MP2)}$ are defined with the MP2 correlation energy of monomer or dimer as

$$E_{fmo1}^{corr(MP2)} = \sum_I E_I^{corr(MP2)}, \quad (4.4.3)$$

$$E_{fmo2}^{corr(MP2)} = \sum_I E_I^{corr(MP2)} + \sum_{I>J} \Delta E_{IJ}^{corr(MP2)}, \quad (4.4.4)$$

where $\Delta E_{IJ}^{corr(MP2)}$ is

$$\Delta E_{IJ}^{corr(MP2)} = E_{IJ}^{corr(MP2)} - E_I^{corr(MP2)} - E_J^{corr(MP2)}. \quad (4.4.5)$$

The IFIE of MP2 is evaluated as

$$\Delta E_{IJ}^{MP2} = \Delta E_{IJ}^{HF} + \Delta E_{IJ}^{corr(MP2)}. \quad (4.4.6)$$

4.4.2 BSSE correction

As is the case with HF calculation, the BSSE is estimated only for the IFIE of the pair not sharing the basis set under the vacuum condition. For BSSE correction, the following values are additionally needed:

$E_{I(IJ)}^{corr(MP2)(vac)}$: the monomer correlation energy of the I -th fragment under the vacuum condition including the basis set of the J -th fragment.

$E_{J(IJ)}^{corr(MP2)(vac)}$: the monomer correlation energy of the J -th fragment under the vacuum condition including the basis set of the I -th fragment.

$E_I^{corr(MP2)(vac)}$: the monomer correlation energy of the I -th fragment under the vacuum condition.

$E_J^{corr(MP2)(vac)}$: the monomer correlation energy of the J -th fragment under the vacuum condition.

With these values, the BSSE of the IFIE of the fragments I and J is written as the following equation:

$$E_{IJ}^{BSSE(corr(MP2))} = \left\{ E_{I(IJ)}^{corr(MP2)(vac)} - E_I^{corr(MP2)(vac)} \right\} + \left\{ E_{J(IJ)}^{corr(MP2)(vac)} - E_J^{corr(MP2)(vac)} \right\} \quad (4.4.7)$$

Thus, the corrected IFIE is

$$\Delta E_{IJ}^{MP2-CP} = \Delta E_{IJ}^{HF-CP} + \left\{ \Delta E_{IJ}^{corr(MP2)} - E_{IJ}^{BSSE(corr(MP2))} \right\} \quad (4.4.8)$$

4.4.3 SCS-MP2 energy

In the case using the spin-component scaled MP2 (SCS-MP2), the monomer or dimer correlation energy scaled with specific factor is used instead of the normal correlation energy. In this text, the superscript of "MP2" is replaced as follows:

In the case using Grimm's factor : $MP2 \rightarrow SCS1-MP2$

In the case using Jung's factor : $MP2 \rightarrow SCS2-MP2$

In the case using Hill's factor : $MP2 \rightarrow SCS3-MP2$

4.4.4 Gradient

Derivative of the FMO2-MP2 energy is

$$\frac{\partial}{\partial A} E_{fmo2}^{MP2} = \frac{\partial}{\partial A} E_{fmo2}^{HF} + \frac{\partial}{\partial A} E_{fmo2}^{corr(MP2)}, \quad (4.4.9)$$

where the term of the MP2 correlation energy $E_{fmo2}^{corr(MP2)}$ is written with the derivatives of the monomer and dimer correlation energy as

$$\frac{\partial}{\partial A} E_{fmo2}^{corr(MP2)} = -(N_f - 2) \sum_I \frac{\partial}{\partial A} E_I^{corr(MP2)} + \sum_{I>J} \frac{\partial}{\partial A} E_{IJ}^{corr(MP2)}. \quad (4.4.10)$$

The derivatives of the monomer and dimer correlation energy is

$$\begin{aligned} \frac{\partial}{\partial A} E_I^{corr} = & \sum_{\mu\nu \in I} D_{I\mu\nu}^{corr} \frac{\partial}{\partial A} h_{I\mu\nu} + \sum_{\mu\nu \in I} W_{I\mu\nu}^{corr} \frac{\partial}{\partial A} S_{I\mu\nu} \\ & + \sum_{\mu\nu\lambda\sigma \in I} \Gamma_{I\mu\nu\lambda\sigma}^{corr} \frac{\partial}{\partial A} (\mu\nu | \lambda\sigma), \end{aligned} \quad (4.4.11)$$

$$\begin{aligned} \frac{\partial}{\partial A} E_{IJ}^{corr} = & \sum_{\mu\nu \in IJ} D_{IJ\mu\nu}^{corr} \frac{\partial}{\partial A} h_{IJ\mu\nu} + \sum_{\mu\nu \in IJ} W_{IJ\mu\nu}^{corr} \frac{\partial}{\partial A} S_{IJ\mu\nu} \\ & + \sum_{\mu\nu\lambda\sigma \in IJ} \Gamma_{IJ\mu\nu\lambda\sigma}^{corr} \frac{\partial}{\partial A} (\mu\nu | \lambda\sigma) + \sum_{\mu\nu \in IJ} D_{IJ\mu\nu}^{corr} \frac{\partial}{\partial A} V_{\mu\nu}^{IJ}, \end{aligned} \quad (4.4.12)$$

where the matrixes of D_X^{corr} , W_X^{corr} , and Γ_X^{corr} are evaluated by the same way as a normal MP2 gradient calculation (the superscript "(MP2)" is omitted). Note that only the derivative of the dimer correlation energy includes the environmental electrostatic potential term. In the case that external electrostatic potential exists, the following term is added:

$$-(N_f - 2) \sum_I \sum_{\mu\nu \in I} D_{I\mu\nu}^{corr(MP2)} \frac{\partial}{\partial A} V_{\mu\nu}^{ext} + \sum_{I < J} \sum_{\mu\nu \in IJ} D_{IJ\mu\nu}^{corr(MP2)} \frac{\partial}{\partial A} V_{IJ\mu\nu}^{ext} \quad (4.4.13)$$

4.4.5 Electron density

Electron density of the FMO2-MP2 is

$$\rho_{fmo2}^{MP2}(\mathbf{r}_m) = \rho_{fmo2}^{HF}(\mathbf{r}_m) + \rho_{fmo2}^{corr(MP2)}(\mathbf{r}_m), \quad (4.4.14)$$

where the correlation term is written as

$$\begin{aligned} \rho_{fmo2}^{corr(MP2)}(\mathbf{r}_m) = & \sum_I \sum_{\mu\nu \in I} D_{I\mu\nu}^{corr(MP2)} \mu(\mathbf{r}_m) \nu(\mathbf{r}_m) \\ & + \sum_{I < J} \sum_{\mu\nu \in X} \Delta D_{IJ\mu\nu}^{corr(MP2)} \phi_\mu(\mathbf{r}_m) \phi_\nu(\mathbf{r}_m). \end{aligned} \quad (4.4.15)$$

where $\Delta \mathbf{D}_{IJ}^{corr(MP2)}$ is defined as

$$\Delta \mathbf{D}_{IJ}^{corr(MP2)} = \mathbf{D}_{IJ}^{corr(MP2)} - \mathbf{D}_I^{corr(MP2)} - \mathbf{D}_J^{corr(MP2)} \quad (4.4.16)$$

4.4.6 Electrostatic potential

Electrostatic potential of the FMO2-MP2 is

$$\phi_{fmo2}^{MP2}(\mathbf{r}_m) = \phi_{fmo2}^{HF}(\mathbf{r}_m) + \phi_{fmo2}^{corr(MP2)}(\mathbf{r}_m), \quad (4.4.17)$$

where the MP2 correlation term is written as

$$\begin{aligned} \phi_{fmo2}^{corr(MP2)}(\mathbf{r}_m) = & \sum_I Tr(\mathbf{D}_I^{corr(MP2)} \mathbf{u}_I(\mathbf{r}_m)) \\ & + \sum_{I > J} Tr(\Delta \mathbf{D}_{IJ}^{corr(MP2)} \mathbf{u}_{IJ}(\mathbf{r}_m)). \end{aligned} \quad (4.4.18)$$

4.4.7 Electric field

Electric field of the FMO2–MP2 is

$$\mathbf{E}_{fmo2}^{MP2}(\mathbf{r}_m) = \mathbf{E}_{fmo2}^{HF}(\mathbf{r}_m) + \mathbf{E}_{fmo2}^{corr(MP2)}(\mathbf{r}_m) \quad (4.4.19)$$

where the correlation term is written as

$$\begin{aligned} \mathbf{E}_{fmo2}^{corr(MP2)}(\mathbf{r}_m) = & - \sum_I Tr \left\{ \mathbf{D}_I^{corr(MP2)} \left(\frac{\partial}{\partial \mathbf{r}_m} \mathbf{u}_I(\mathbf{r}_m) \right) \right\} \\ & - \sum_{I>J} Tr \left\{ \Delta \mathbf{D}_{IJ}^{corr(MP2)} \left(\frac{\partial}{\partial \mathbf{r}_m} \mathbf{u}_{IJ}(\mathbf{r}_m) \right) \right\}. \end{aligned} \quad (4.4.20)$$

4.4.8 Mulliken population

Mulliken population of the FMO2–MP2 is

$$N_{fmo2}^{MP2}(A) = N_{fmo2}^{HF}(A) + N_{fmo2}^{corr(MP2)}(A) \quad (4.4.21)$$

where the correlation term is written as

$$\begin{aligned} N_{fmo2}^{corr(MP2)}(A) = & \sum_I \sum_{\mu \in A} (\mathbf{D}_I^{corr(MP2)} \mathbf{S}_I)_{\mu\mu} \\ & + \sum_{I>J} \sum_{\mu \in A} (\Delta \mathbf{D}_{IJ}^{corr(MP2)} \mathbf{S}_{IJ})_{\mu\mu}. \end{aligned} \quad (4.4.22)$$

4.5 FMO–RI–MP2

In this section, the theory related to the FMO–RI–MP2 is explained, making it be related to the output of the **PAICS**. The formulation basically follows the previous publications reporting the theory and method of the FMO scheme [19, 20, 21].

4.5.1 Energy

The RI–MP2 total energy of one-body approximation (FMO1–RI–MP2) and two-body approximation (FMO–RI–MP2) is

$$E_{fmo1}^{RI-MP2} = E_{fmo1}^{HF} + E_{fmo1}^{corr(RI-MP2)}, \quad (4.5.1)$$

$$E_{fmo2}^{RI-MP2} = E_{fmo2}^{HF} + E_{fmo2}^{corr(RI-MP2)}. \quad (4.5.2)$$

Here, $E_{fmo1}^{corr(RI-MP2)}$ and $E_{fmo2}^{corr(RI-MP2)}$ are defined with the RI–MP2 correlation energy of monomer or dimer as

$$E_{fmo1}^{corr(RI-MP2)} = \sum_I E_I^{corr(RI-MP2)}, \quad (4.5.3)$$

$$E_{fmo2}^{corr(RI-MP2)} = \sum_I E_I^{corr(RI-MP2)} + \sum_{I>J} \Delta E_{IJ}^{corr(RI-MP2)}, \quad (4.5.4)$$

where $\Delta E_{IJ}^{corr(RI-MP2)}$ is

$$\Delta E_{IJ}^{corr(RI-MP2)} = E_{IJ}^{corr(RI-MP2)} - E_I^{corr(RI-MP2)} - E_J^{corr(RI-MP2)}. \quad (4.5.5)$$

The IFIE of MP2 is evaluated as

$$\Delta E_{IJ}^{RI-MP2} = \Delta E_{IJ}^{HF} + \Delta E_{IJ}^{corr(RI-MP2)}. \quad (4.5.6)$$

4.5.2 BSSE correction

The BSSE correction in the FMO-RI-MP2 is evaluated by the exactly same way as that in the FMO-MP2. Thus, the discussion and formulaton are obtained by the following replacement of the superscript in the section 4.4.2:

$$MP2 \rightarrow RI-MP2$$

4.5.3 Gradient

The derivative of the FMO2-RI-MP2 energy is

$$\frac{\partial}{\partial A} E_{fmo2}^{RI-MP2} = \frac{\partial}{\partial A} E_{fmo2}^{HF} + \frac{\partial}{\partial A} E_{fmo2}^{corr(RI-MP2)}, \quad (4.5.7)$$

where derivative of the RI-MP2 correlation energy $E_{fmo2}^{corr(RI-MP2)}$ is written with the derivative of the monomer or dimer RI-MP2 correlation energy as

$$\frac{\partial}{\partial A} E_{fmo2}^{corr(RI-MP2)} = -(N_f - 2) \sum_I \frac{\partial}{\partial A} E_I^{corr(RI-MP2)} + \sum_{I>J} \frac{\partial}{\partial A} E_{IJ}^{corr(RI-MP2)}. \quad (4.5.8)$$

the derivative of the monomer and dimer correlation energy is

$$\begin{aligned} \frac{\partial}{\partial A} E_I^{corr} = & 4 \sum_{\mu\nu P \in I} \Gamma_{I P \mu\nu}^{corr} \frac{\partial}{\partial A} (P | \mu\nu) - 2 \sum_{PQ \in I} \gamma_{I PQ}^{corr} \frac{\partial}{\partial A} (P | Q) \\ & - 2 \sum_{\mu\nu \in I} D_{I \mu\nu}^{corr} \frac{\partial}{\partial A} h_{\mu\nu}^I - 2 \sum_{\mu\nu \in I} W_{I \mu\nu}^{corr} \frac{\partial}{\partial A} S_{\mu\nu}^I \\ & + 2 \sum_{\mu\nu\lambda\sigma \in I} (2D_{I \mu\nu}^{corr} D_{I \lambda\sigma}^{HF} - D_{I \mu\sigma}^{corr} D_{I \lambda\nu}^{HF}) \frac{\partial}{\partial A} (\mu\nu | \lambda\sigma), \end{aligned} \quad (4.5.9)$$

$$\begin{aligned} \frac{\partial}{\partial A} E_{IJ}^{corr} = & 4 \sum_{\mu\nu P \in IJ} \Gamma_{IJ P \mu\nu}^{corr} \frac{\partial}{\partial A} (P | \mu\nu) - 2 \sum_{PQ \in IJ} \gamma_{IJ PQ}^{corr} \frac{\partial}{\partial A} (P | Q) \\ & - 2 \sum_{\mu\nu \in IJ} D_{IJ \mu\nu}^{corr} \frac{\partial}{\partial A} h_{\mu\nu}^{IJ} - 2 \sum_{\mu\nu \in IJ} W_{IJ \mu\nu}^{corr} \frac{\partial}{\partial A} S_{\mu\nu}^{IJ} + \sum_{\mu\nu \in IJ} D_{IJ \mu\nu}^{corr} \frac{\partial}{\partial A} V_{\mu\nu}^{IJ} \\ & + 2 \sum_{\mu\nu\lambda\sigma \in IJ} (2D_{IJ \mu\nu}^{corr} D_{IJ \lambda\sigma}^{HF} - D_{IJ \mu\sigma}^{corr} D_{IJ \lambda\nu}^{HF}) \frac{\partial}{\partial A} (\mu\nu | \lambda\sigma), \end{aligned} \quad (4.5.10)$$

where the matrixes of D_X^{corr} , W_X^{corr} , Γ_X^{corr} , and γ_X^{corr} are calculated by the same way as a normal RI-MP2 gradient calculation (the superscript " $(RI-MP2)$ " is omitted). Note that derivative of the dimer RI-MP2 correlation energy includes the environmental electrostatic potential term. In the case that external electrostatic potnetial exists, the following term is added:

$$-(N_f - 2) \sum_I \sum_{\mu\nu \in I} D_{I \mu\nu}^{corr(RI-MP2)} \frac{\partial}{\partial A} V_{I \mu\nu}^e + \sum_{I<J} \sum_{\mu\nu \in IJ} D_{IJ \mu\nu}^{corr(RI-MP2)} \frac{\partial}{\partial A} V_{IJ \mu\nu}^e \quad (4.5.11)$$

4.5.4 Electron Density

Electron density of the FMO2–RI–MP2 is

$$\rho_{fmo2}^{RI-MP2}(\mathbf{r}_m) = \rho_{fmo2}^{HF}(\mathbf{r}_m) + \rho_{fmo2}^{corr(RI-MP2)}(\mathbf{r}_m), \quad (4.5.12)$$

where the correlation term is written as

$$\begin{aligned} \rho_{fmo2}^{corr(RI-MP2)}(\mathbf{r}_m) = & \sum_I \sum_{\mu\nu \in I} D_I^{corr(RI-MP2)} \mu(\mathbf{r}_m) \nu(\mathbf{r}_m) \\ & + \sum_{\mu\nu \in X} \Delta D_{IJ}^{corr(RI-MP2)} \mu(\mathbf{r}_m) \nu(\mathbf{r}_m). \end{aligned} \quad (4.5.13)$$

where $\Delta \mathbf{D}_{IJ}^{corr(MP2)}$ is defined as

$$\Delta \mathbf{D}_{IJ}^{corr(RI-MP2)} = \mathbf{D}_{IJ}^{corr(RI-MP2)} - \mathbf{D}_I^{corr(RI-MP2)} - \mathbf{D}_J^{corr(RI-MP2)} \quad (4.5.14)$$

4.5.5 Electrostatic potential

The electrostatic potential of the FMO2–RI–MP2 is

$$\phi_{fmo2}^{RI-MP2}(\mathbf{r}_m) = \phi_{fmo2}^{HF}(\mathbf{r}_m) + \phi_{fmo2}^{corr(RI-MP2)}(\mathbf{r}_m), \quad (4.5.15)$$

where the correlation term is written as

$$\begin{aligned} \phi_{fmo2}^{corr(RI-MP2)}(\mathbf{r}_m) = & \sum_I Tr \left(\mathbf{D}_I^{corr(RI-MP2)} \mathbf{u}_I(\mathbf{r}_m) \right) \\ & + \sum_{I>J} Tr \left(\Delta \mathbf{D}_{IJ}^{corr(RI-MP2)} \mathbf{u}_{IJ}(\mathbf{r}_m) \right). \end{aligned} \quad (4.5.16)$$

4.5.6 Electric field

The electric field of the FMO2–MP2 is

$$\mathbf{E}_{fmo2}^{RI-MP2}(\mathbf{r}_m) = \mathbf{E}_{fmo2}^{HF}(\mathbf{r}_m) + \mathbf{E}_{fmo2}^{corr(RI-MP2)}(\mathbf{r}_m) \quad (4.5.17)$$

where the correlation term is written as

$$\begin{aligned} \mathbf{E}_{fmo2}^{corr(RI-MP2)}(\mathbf{r}_m) = & - \sum_I Tr \left\{ \mathbf{D}_I^{corr(RI-MP2)} \left(\frac{\partial}{\partial \mathbf{r}_m} \mathbf{u}_I(\mathbf{r}_m) \right) \right\} \\ & - \sum_{I>J} Tr \left\{ \Delta \mathbf{D}_{IJ}^{corr(RI-MP2)} \left(\frac{\partial}{\partial \mathbf{r}_m} \mathbf{u}_{IJ}(\mathbf{r}_m) \right) \right\}. \end{aligned} \quad (4.5.18)$$

4.5.7 Mulliken population

Mulliken population of the FMO2–RI–MP2 is

$$N_{fmo2}^{RI-MP2}(A) = N_{fmo2}^{HF}(A) + N_{fmo2}^{corr(RI-MP2)}(A) \quad (4.5.19)$$

where the correlation term is written as

$$\begin{aligned} N_{fmo2}^{corr(RI-MP2)}(A) = & \sum_I \sum_{\mu \in A} (\mathbf{D}_I^{corr(RI-MP2)} \mathbf{S}_I)_{\mu\mu} \\ & + \sum_{I>J} \sum_{\mu \in A} (\Delta \mathbf{D}_{IJ}^{corr(RI-MP2)} \mathbf{S}_{IJ})_{\mu\mu}. \end{aligned} \quad (4.5.20)$$

4.6 FMO–LMP2 (energy)

In this section, the theory related to the LMP2 is explained, making it be related to the output of the **PAICS**. The formulation basically follows the previous publications reporting the theory and method of the FMO scheme [23, 24].

4.6.1 Energy

The LMP2 total energy of one-body approximation (FMO1–LMP2) and two-body approximation (FMO–LMP2) is

$$E_{fmo1}^{LMP2} = E_{fmo1}^{HF} + E_{fmo1}^{corr(LMP2)}, \quad (4.6.1)$$

$$E_{fmo2}^{LMP2} = E_{fmo2}^{HF} + E_{fmo2}^{corr(LMP2)}. \quad (4.6.2)$$

Here, $E_{fmo1}^{corr(LMP2)}$ and $E_{fmo2}^{corr(LMP2)}$ are defined with the LMP2 correlatoin energy of the monomer or dimer as

$$E_{fmo1}^{corr(LMP2)} = \sum_I E_I^{corr(LMP2)}, \quad (4.6.3)$$

$$E_{fmo2}^{corr(LMP2)} = \sum_I E_I^{corr(MP2)} + \sum_{I>J} \Delta E_{IJ}^{corr(LMP2)}, \quad (4.6.4)$$

where $\Delta E_{IJ}^{corr(LMP2)}$ is

$$\Delta E_{IJ}^{corr(LMP2)} = E_{IJ}^{corr(LMP2)} - E_I^{corr(LMP2)} - E_J^{corr(LMP2)}. \quad (4.6.5)$$

The IFIE of the FMO–LMP2 is evaluated as

$$\Delta E_{IJ}^{LMP2} = \Delta E_{IJ}^{HF} + \Delta E_{IJ}^{corr(LMP2)(sum)} \quad (4.6.6)$$

Here, $\Delta E_{IJ}^{corr(LMP2)(sum)}$ is calculated using the pair correlation energies between local orbitals of the dimer LMP2 calculation as

$$\Delta E_{IJ}^{corr(LMP2)(sum)} = \sum_{i \in I} \sum_{j \in J} \epsilon_{ij} \quad (4.6.7)$$

Here, ϵ_{ij} is the pair correlation energy. Thus, we can define the correlation energy of the FMO2–LMP2 as

$$E_{fmo2}^{corr(LMP2)(sum)} = \sum_I E_I^{corr(MP2)} + \sum_{I>J} \Delta E_{IJ}^{corr(LMP2)(sum)}. \quad (4.6.8)$$

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